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(54) DEVICE AND METHOD FOR THE ELECTROCHEMICAL DEPOSITION OF CHEMICAL COMPOUNDS AND ALLOYS WITH CONTROLLED COMPOSITION AND/OR STOICHIOMETRY

VORRICHTUNG UND VERFAHREN FÜR DIE GALVANISCHE ABSCHEIDUNG VON CHEMISCHEN ELEMENTEN UND LEGIERUNGEN MIT KONTROLLIERTER ZUSAMMENSETZUNG UND/ODER STÖCHIOMETRIE

DISPOSITIF ET PROCÉDÉ POUR LE DÉPÔT ÉLECTROCHIMIQUE DE COMPOSÉS ET ALLIAGES CHIMIQUES AVEC UNE COMPOSITION ET/OU UNE STOECHIOMÉTRIE CONTRÔLÉE

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Description

TECHNICAL FIELD

[0001] The presented invention relates to a method for depositing an alloy and/or chemical compounds on a substrate immersed in an electrolyte. It furthermore relates to the use of such a method for the deposition in particular of $Bi_{2+x}Te_{3-x}$ coatings and it also relates to a specifically tailored device for the above method.

BACKGROUND OF THE INVENTION

[0002] Electrochemical deposition (ECD) is a well-known method to electrochemically deposit layers of metals, alloys or chemical substances on the surface or into a surface structure of a substrate to be treated.

[0003] Electrochemical deposition is thus generally known and can be achieved by a variety of techniques. A typical electrochemical deposition method comprises the reduction of ions from aqueous, organic or fused salt electrolytes at the electrode-electrolyte interface forming a deposition. This deposition can be achieved in two different ways : a) with an electroless (autocatalytic) deposition process in which the electrons are supplied by a reducing agent in the electrolyte or b) by means of electrodeposition in which the an external power supply is the electron source.

[0004] In this context, so-called current controlled ECD-processes (galvanostatic ECD) are known, in which the deposition process is carried out under complete current control. This means that if for example a pulse sequence is used for the deposition process, there are intervals of time in which a high amplitude current is established and maintained (deposition period), and there are intervals in which a low amplitude current is established and maintained (relaxation or off-time period).

[0005] In contrast to this there are so-called voltage controlled ECD-processes (potentiostatic ECD), in which the deposition process is carried out under complete voltage control. This means that if for example a pulse sequence is used for the voltage controlled deposition process, there are intervals of time in which a potential, at which the deposition of the desired material takes place, is established and maintained (deposition period) and there are intervals in which a potential, where no or less deposition or dissolution of the desired material takes place, is established and maintained (relaxation or off-time period).

[0006] For the deposition of certain alloy and compounds using conventional electrochemical deposition processes may lead to problematic layer properties and material properties like for example insufficient adhesion, internal stress or undesired physical properties etc. These problems are due to variations in the stoichiometry/composition across the thickness of the layer which in turn are due to lack of control during the deposition process. This insufficient stoichiometric control during the deposition is inherent to the processes according to the state-of-the-art.

[0007] The above voltage controlled pulsed electrochemical deposition allows to quite efficiently control the deposition reactions during the deposition period. However, during the relaxation period for certain electrochemical systems, e.g. $Bi_{2+x}Te_{3-x}$ the problem of undesired reactions on the deposition electrode occurs, which are caused by shifting of the equilibrium potential. These undesired reactions are characterised by a current flow from or to the external voltage source, indicating oxidation or reduction processes. The result of these undesired processes is a changing composition and correspondingly changing properties of the deposited layer.

[0008] The current controlled pulsed electrochemical deposition is problematic in the sense that the deposition processes during the deposition period cannot be completely controlled. The reason for this is that there can be variations in the potential at the deposition electrode leading in turn to changes in the stoichiometry and the composition of the generated layer. These variations of the potential are caused on the one hand by changes of the deposition surface area, which for example may be caused by changes in surface roughness of the deposit or design imposed changes of the electrode geometry, and on the other hand due to the change of the electrical resistance of the deposited layer with increasing thickness of the deposited layer.

[0009] One possible application of ECD is the fabrication of thermoelectric devices in particular the formation of its thermocouples. A material’s suitability for thermoelectric conversion may be expressed in terms of the thermoelectric figure of merit ZT that is defined as $\alpha^2\sigma T/\lambda$ where α is the Seebeck coefficient, σ is the electrical conductivity, T is the mean absolute temperature and λ is the thermal conductivity of the material. The V_2-VI_3 compound bismuth telluride (Bi_2Te_3) is considered to have the highest ZT in the regime near room temperature. Bi_2Te_3 is a semiconducting compound which may show either n-type or p-type behaviour depending on slight variations of the stoichiometry. It was shown that $Bi_{2+x}Te_{3-x}$ is a p-type material, i.e. has a positive Seebeck coefficient, for $x > 0$. In this case the Bi_2Te_3 is said to be "*Bi rick*". For "*Te rich*" material($x < 0$), the Seebeck coefficient is negative. This property reflects a substantial advantage when building thermocouples because the p- and n-legs can be made of materials with near identical mechanical and thermal properties.

[0010] The interest in ECD of Bi_2Te_3 is steadily growing because of its potential for low cost microfabrication with high deposition rates. Moreover the possibility to selectively electroplate material into patterned photoresist molds is beneficial for the integrated fabrication of micro thermoelectric devices. In addition, ECD into porous alumina membranes has been successfully applied for the fabrication of Bi_2Te_3 nanowire arrays, for which enhanced thermoelectric properties compared to bulk material have been theoretically predicted.

[0011] In the existing studies on ECD of Bi_2Te_3 the material was deposited either galvanostatically, potientiostatically or by electroless plating.

[0012] Until now, all measurements of un-doped Bi_2Te_3 have yielded negative Seebeck coefficients even though some samples were Bi rich. Unfortunately few measurements have been made to investigate the stoichiometry across the thickness of electrochemically deposited Bi_2Te_3 layers. However discrepancies illustrate the necessity of investigations on the stoichiometric profile and of means to control the deposition process in such a way, that a homogeneous stoichiometry is achieved throughout the entire layer.

[0013] As it is intended to use the electrodeposited material for fabrication of integrated micro thermoelectric generators, a thickness of about 300 μm is necessary to achieve optimized devices. The thickest ever reported layer was 350μm and was plated with a rate of 7.3 μm/h. The highest rate for ECD of Bi_2Te_3 reported was 20 μm/h. Application of pulsed deposition enhances deposition control and quality of the deposit. Interrupting the current supports the replenishment of the ion concentration at the working electrode. As a consequence higher current densities can be applied during the deposition pulse. Hence the nucleation rate is increased which leads to a refined morphology and reduced roughness. Deposits of higher density with fewer inclusions and less impurities could be achieved. Improvements in adhesion and hardness of deposits are reported.

[0014] Although the limiting current density of an electrolyte may not be increased by pulse plating, higher overall deposition rates compared to continuous plating may practically be achieved due to the improved deposit properties of pulse plated deposits which allow application of a higher average current density.

[0015] Finally for the deposition of compounds and alloys like of Bi_2Te_3, the increased current densities achievable with pulse plating allow shifting the ratio of rates of reactions with different kinetics to an extent, which is not possible with continuous plating providing thereby additional control over the stoichiometric composition of the deposited compound.

[0016] The document "Microstructure of Ni-Cu multilayers electrodeposited from a citrate electrolyte" by Ch. Bonhote et al. (Electrochimica Acta, Vol. 42, No 15, pp 2407-2417) pertains to a method of electrodeposition. Is however silent about BiTe-systems. The method is disclosed is working with a reference electrode (calomel, page 2408, second column) and is strictly only working with constant current (galvanostatic method). There is no disclosure of pulse sequences or the like, no disclosure of periods in which the voltage is controlled to be at a defined level with respect to the reference electrode. The document "Study of electrodeposition of bismuth telluride by voltametric methods and in-situ electrochemical quartz crystal microbalance method" by Li et al. (Thin Solid Films 515 (2007), 7847-7854) in the whole first part is disclosing purely constant voltage controlled processes using three electrodes. In different time spans different voltages are used.

SUMMARY OF THE INVENTION

[0017] The object of the present invention is therefore to provide an improved method of electrochemical deposition.

[0018] The proposed method for depositing an alloy and/or chemical compounds on a substrate immersed in a liquid electrolyte, comprises the steps of:

I. applying a first constant or varying potential to the substrate under voltage control for a deposition time interval (t_A);
II. applying a second constant or varying current to the substrate under current control for a relaxation time interval (t_B);

repeating the sequence of steps I.-II. at least twice.

[0019] The steps I. and II. may consist of a series of time intervals with different potential or current, respectively. Within the intervals the potential/current can be varied as a function of time (shaped pulses) or it can be constant (rectangular pulses).

[0020] The present invention therefore relates to a new method for the electrochemical deposition of chemical compounds or alloys. One of the key features of the invention is that a sequence of voltage controlled deposition periods or deposition pulses alternating with current controlled relaxation periods or relaxation pulses is used. This however does not exclude that there is additional pulses which can be voltage controlled and/or current controlled.

[0021] More specifically and as outlined in more detail further below, the above steps can be realised, according to a first preferred embodiment, by using a reference electrode (RE) or a pseudo-reference electrode, a working electrode (WE) and a counter electrode (CE) which are immersed in the liquid electrolyte (1). Using this system the above two steps are carried out as follows:

During step I. the potential is controlled to be constant, or controlled to be variable according to a predefined time dependency of the potential. This means that this potential is controlled between the reference electrode (RE) or pseudo-reference electrode and the working electrode (WE). It in turn means that the working electrode (WE) is kept at an absolutely controlled (constant) voltage level with respect to the electrolyte, while the potential between the working electrode (WE) and the counter electrode (CE) is allowed to vary and adapt as a function of time. Graphically the time dependency during this first time interval t_A is illustrated in the figures, in particular in figure 14 and will be discussed in more detail below. One however notes that the current (upper part of figure 14) as flowing between the working electrode (WE) and the counter electrode (CE) is adapting to the constant voltage applied between the reference electrode (RE) and the working electrode (lower part of figure 14).

During step II. the current is controlled to be constant, or controlled to be variable according to a predefined time dependency of the current, between the working electrode (WE) and the counter electrode (CE). The voltage between reference electrode (RE) and the working electrode (WE) is concomitantly allowed to vary as a function of time and to adapt to this situation while not becoming zero.

[0022] Normally therefore, for carrying out the method a three-electrode system is used, including a reference electrode, a working electrode and a counter electrode. During step I. the potential is controlled between reference electrode (RE or a pseudo-reference electrode) and working electrode (WE), which means that voltage control is not meaning keeping constant the voltage difference between the counter electrode (CE) and (WE) as the case for voltage controlled deposition with a conventional two electrode system as known in the state-of-the-art, but to keep the working electrode at an absolutely controlled voltage level with respect to the electrolyte. During step I., as there is an infinitely high resistance between RE and WE, no current is flowing between RE and WE but only between WE and CE. During step II. the current is controlled to be constant between WE and CE, while the voltage between RE and WE adapts to this situation. It is important to note that the voltage does not switch to zero during this step but decays as a function of time as illustrated in figure 3d and as illustrated in figure 14, switching to zero would lead to dissolution during the relaxation time. It is therefore important to note that during step II. the voltage between RE and WE is not simply zero but adapts to the desired value of I between WE and CE. For the case where the current between WE and CE is controlled to be at a value different from zero (feedback loop) indeed the current is controlled by shifting V between RE and WE are such that the current is at the desired value. For the case where the current is set to zero by simply disconnecting the path between RE and CE, the voltage between RE and WE starts at the initial value (terminal value of the preceding interval of step I.) and is allowed to decay in as far as naturally occurring in the system, so it adapts to the situation that I = 0, see figure 3d, discussed in more detail below.

[0023] With the proposed mixed method it is possible to control the stoichiometry over the entire thickness of a deposition, and indeed since the deposition potential is crucial and needs to be in a defined range, the control of the morphology of the deposit can only be achieved by the pulse duration as proposed. However, reducing pulse duration may have side effects to the deposit, like stoichiometry changes, adhesion problems, strain and/or reduced deposition rates.

[0024] Our invention allows to reduce the current flow between the working electrode and the counter electrode in a controlled manner, while the potential control between working electrode and reference electrode remains unimpaired and controllable. This current control can for example be achieved by introducing a variable resistance between the working electrode and the counter electrode. With increasing resistivity, a decrease in the deposition rate occurs but also an increase in material homogeneity can be observed. This level of deposition quality could not be reached by only reducing the pulse duration, since short but high current pulses lead to inhomogeneous deposits. According to a preferred embodiment of the invention therefore, control in particular during step I, so in the deposition step, takes place using an adaptable and controllable resistance between the working electrode and the counter electrode, wherein preferably control of this resistance is effected using a feedback loop by current measurement in the path between working electrode and counter electrode. This resistance allows to finely control the current flow (not just determined anymore by the diffusion in the solution) and allows to slow down the deposition process within one pulse without changing the applied voltage, which in turn leads to superior morphology, less grains, better surface roughness.

[0025] To control the current, one or more constant or variable resistances can thus be used. Good results have been obtained, for a variable resistance controlled over a feedback loop (e.g. a PID-controller), where the current was sensed and kept at a desired level. However, other application concepts are possible, where the desired level is not constant but changing over time in a well controlled manner, to obtain materials with different mechanical, electrical or physical properties.

[0026] From a general point of view the following explanation shall serve to understand the principles (see also figure 14): In a normal potential controlled deposition pulse, the current increases first to a certain value and then decreases rapidly. This decrease is related to a depletion of the ions around the electrode. This is a so called "diffusive controlled system". By introducing a resistance, the current will be proportionally reduced (in a potential controlled system). As a consequence, the depletion of the ions around the electrode is inhibited or strongly reduced. We actively change the "diffusive controlled system" into a "charge transfer controlled system". As a consequence, the deposition becomes more homogeneous.

[0027] According to a preferred embodiment the sequence consists of voltage controlled deposition periods alternating with current controlled relaxation periods.

[0028] The newly proposed method allows the exact control of the stoichiometry and composition, respectively, over the whole duration of the deposition and therefore allows a targeted control over the layer properties and the material properties over the whole thickness of the layer.

[0029] This is in complete contrast to the state-of-the-art. In the state-of-the-art it is known to have either voltage controlled pulsed electroplating or current controlled electroplating but there is no disclosure of a combination of these two methods. Indeed a standard device can only carry out a strictly voltage controlled pulsed electroplating or a strictly current controlled electroplating and the corresponding control then applied to deposition periods as well as relaxation periods both periods either being voltage controlled or current controlled.

[0030] In this respect it should be pointed out that it is known to have voltage controlled pulsed deposition in which voltage pulses are alternating with so called zero voltage pulses (see e.g. US 6,881,318). If however such a voltage controlled pulse sequence is used for electroplating, inherently during the zero voltage periods there is no current control in a three electrode system. Also with a 2 electrode system there is never full voltage control in the strict sense (although this expression is often used), as control of the voltage between the working electrode and the counter electrode can only control the relative potential between WE and CE but not the relative potential between the working electrode and the electrolyte solution (which is the important quantity for the control of the processes taking place on the working electrode) and correspondingly the relative potential between the working electrode and the counter electrode changes under such an alleged voltage control in an uncontrollable manner as a function of the processes on the electrodes and as a function of the electrolyte solution as these change. Quite in contrast, during the zero voltage periods an important current is flowing and this flowing current is actually changing as a function of time and leads to detrimental effects as outlined in the introductory portion and as experimentally demonstrated in the detailed description below.

[0031] As discussed, the newly proposed method allows an exact control of the stoichiometry and the composition over the whole deposition process and therefore over the whole thickness of the deposited layer. This control is made possible by the use of the above-mentioned sequence including voltage controlled deposition and current controlled relaxation.

[0032] Indeed the voltage controlled deposition period allows to establish the desired electrochemical reduction and allows complete control over the composition and structure and correspondingly over the properties of the deposited material. On the other hand the current controlled relaxation period allows current-free compensation and leveling reactions at the interface between the already deposited material (electrode) and the electrolyte, which leads to a self-regulated resting potential.

[0033] So far the problems of with insufficient control of the deposit's composition and or stoichiometry during ECD according to the state-of-the-art were avoided by using different methods of deposition like for example sputtering, evaporation or deposition from the gas phase, accepting the specific disadvantages of these methods when comparing them with electroplating. Compared to the state-of-the-art the electrochemical electroplating as proposed allows however to completely control the layer properties and the material properties, including optical, electrical, physical properties etc.

[0034] In a first preferred embodiment of the present invention, during the first time interval (t_A) the voltage is controlled to be constant (ie rectangular pulses), preferably within a tolerance range of at most ±0.1 V, most preferably within a tolerance range of at most $\pm 500 \mu V$.

[0035] According to a further preferred embodiment, during the second interval (t_B) the current is kept constant (ie "rectangular" relaxation period), preferably within a tolerance range equivalent to a current density on the substrate of at most $\pm 10 mA/cm^2$, most preferably within a tolerance range of at most $\pm 1 \mu A/cm^2$.

[0036] Preferably, during the second interval (t_B) the current is at zero (I=0), preferably within a tolerance range equivalent to a current density on the substrate of at most $\pm 10 mA/cm^2$, most preferably within a tolerance range of at most $\pm 1 \mu A/cm^2$.

[0037] It is for example possible to run the process such that during the first time interval (t_A) the absolute value of the voltage is above the nucleation potential of the reacting substance, typically at least 0.1 V (e.g. for $Bi_{2+x}Te_{3-x}$ ca. -0.25 V), preferably in the range of 0.1 - 3.0V (always in the following with reference to a mercury standard electrode, MSE), preferably in the range of 0.4 - 1.0V. Typically the first time interval (t_A) is in the range of 1 μs-60s, preferably in the range of 1 ms-1s, most preferably in the range of 1-200 ms.

[0038] As concerns the second time interval (t_B) it is according to a further embodiment in the range of 1 μs-60 s, preferably in the range of 1 ms-30s, most preferably in the range of 1-5s.

[0039] Generally one can say that it is preferred that the duty cycle of the first time interval (t_A) to the second time interval (t_B) is below 80% or below 50%, preferably below 25%, most preferably below 10% (a duty cycle of less than 50% meaning that the length of the first time interval is smaller than the length of the second time interval, and a duty cycle of less than 25% meaning that the length of the first time interval is smaller than three times the second time interval etc.).

[0040] As outlined above, the proposed method allows to control the stoichiometry of the deposited alloy and/or a chemical compound. This control is possible by means of at least one correspondingly adapted process parameter selected from the following group: value of voltage and/or length (t_A) of the first time interval; ionic concentration ratio of the starting materials of the compound dissolved as ions in the electrolyte.

[0041] The present invention also pertains to the use of the above methods for depositing a semiconducting material, a thermoelectric material, and/or a magnetic material, preferably on the basis of at least one of the materials selected from the following group: $Bi_{2+x}Te_{3-x}$, CuInSe, BiSbTe, BiSeTe, SbTe, GeTe, AgSe, PbTe, TeAgGeSb, AgSb, SnTe, CuSe, ZnHgSe, PbCd or CdTe, CiNiFe or CoFe onto a substrate. This however does not exclude the applicability of the proposed method to the deposition of other materials.

[0042] For depositing $Bi_{2+x}Te_{3-x}$, is preferred that the voltage during the first time interval (t_A) is selected in the range (-10.0) - (-0.1)V (again as always vs MSE), preferably (-1.0) - (-0.3)V, and during the second time interval there is a controlled current of I=0.

[0043] The newly proposed method for the first time allows to actually produce p-type $Bi_{2+x}Te_{3-x}$. This is possible by running the process under conditions such that in the electrolyte the ratio of [$HTeO^{2+}$] to [Bi^{3+}] is chosen such that the atomic ratio Te : Be in the deposit is below 1.6, or below 1.5, or below 1.25 (angular brackets as usual standing for concentrations). In some cases this can be the threshold ratio also of the concentrations of the ions [$HTeO^{2+}$] to [Bi^{3+}] in the electrolyte.

[0044] According to a further preferred embodiment of the method and the use, the electrolyte solution comprises at least 1.5M [HNO_3], at least 30mM [$HTeO^{2+}$] and/or preferably at least 30mM [Bi^{3+}]. Indeed it is possible to achieve these exceedingly high concentrations of relevant constituents, allowing to have, in combination with the proposed method, the extremely high deposition rates which are by a factor of more than two higher than the deposition rates according to the state-of-the-art and as discussed below and to enable to produce very thick layers in the millimeter range.

[0045] The preparation of the liquid electrolyte is an important aspect for being able to control the deposition process and to generate homogeneous layers. Indeed to have a sufficiently high concentration of the necessary systems for deposition can sometimes be essential for being able to effectively carry out the process. The present invention therefore in addition to the above relates to a method for making a liquid electrolyte solution, to such an electrolyte solution as such, and to a method for preparing such a liquid electrolyte solution prior to carrying out the above method. According to this aspect of the invention, the liquid electrolyte is prepared by providing a concentrated HNO_3 solution, typically in a concentration of more than 70 %, heating it until reaching or just below boiling point, typically until not more than 40° below boiling point, preferably not more than 5° below boiling point. Subsequently of TeO_2 is added in the desired amount, the system is stirred and water is slowly added to the solution until essentially complete dissolution of TeO_2. This is followed by an optional decrease of temperature to below 80° (active cooling or allowing to cool down), addition of BiO_3 in the desired amount, stirring until essentially complete dissolution of all constituents (during this period the solution may be heated, up to boiling temperature, also water addition is possible during this step for complete dissolution), addition of water until reaching a desired HNO_3 concentration, preferably of in the range of 2M.

[0046] More specifically, a highly concentrated HNO_3 (76%) solution is provided, is heated until reaching boiling temperature or just below its boiling point, TeO_2 is added followed by a stirring and successive water addition until essentially complete dissolution of TeO_2; optional decrease temperature to below 80°; add BiO_3, stir and wait until dissolved; add water until reaching 2M HNO_3.

[0047] Furthermore the present invention relates to a device for use in a method as outlined above or for a specific use as outlined above. This device comprises a power supply and mixed method control unit to connect to at least one working electrode ,at least one counter electrode and (optionally) one or more additional (reference-) electrodes. For the voltage controlled periods the use of a reference electrode allows to have more simple and more accurate control. The mixed method control unit comprises a voltage source for providing a controlled voltage to the electrodes and at least one controllable triggered switch (e.g. mechanical, electromechanical, IC or electrical triggered switch) which allows to connect and disconnect the voltage source from the electrodes for the first time interval and the second time interval, respectively. Such as a device typically further comprises a reference electrode (RE) or a pseudo-reference electrode connected with the working electrode (WE) and an element for measurement and/or control of the voltage between the reference electrode (RE) and the working electrode (WE). Optionally the unit further comprises at least one current source for providing a controlled current to the electrodes and/or at least one short-circuit pathway and/or at least one open circuit pathway, all of these elements connectable and disconnectable by the at least one controllable triggered switch alternatively to the voltage source. It preferably furthermore comprises a control unit and means for monitoring the process.

[0048] Further embodiments of the present invention are outlined in the dependent claims.

SHORT DESCRIPTION OF THE FIGURES

[0049] In the accompanying drawings preferred embodiments of the invention and measurements are shown in which:

Figure 1	are cyclic voltammograms of Pt recorded in 2M HNO_3 + 80 mM $HTeO_2^+$ + 40 mM Bi^{3+} (dashed line), 60 mM Bi^{3+} (solid line), 90 mM Bi^{3+} (doted line) and 110 mM Bi^{3+} (dash doted line) respectively, scan speed: 10mV/s;
Figure 2	a) Pulse form of voltage pulses for chronoamperometric investigation, deposition pulses: -0.72V vs. MSE 1 s, resting pulses: -0.25 V vs. MSE 20 s b) Current response to a series of potential pulses applied to a Pt electrode in 2 M HNO_3 + 80 mM $HTeO_2^+$ + 110 mM Bi^{3+}. c) Superimposed current response to the deposition pulses d) Enlargement of the current response to the resting pulses;
Figure 3	a) Pulse form of current pulses for chronopotentiometric investigation, deposition pulses: -0.04A 1 s, resting pulses: 0A 20 s b) Voltage response to a series of current pulses applied to a Pt electrode in 2 M HNO_3 + 80 mM $HTeO_2^+$ + 110 mM Bi^{3+}. c) Superimposed voltage response to the deposition pulses. d) Enlargement of the voltage response to the resting pulses;
Figure 4	Linear sweep stripping of previously deposited $Bi_{2+x}Te_{3-x}$ layers recorded in 2M $HNO_3$with a scan speed of 10mV/s. The deposition of the layers had been done with the mixed method with 1, 4 and 16 deposition pulses respectively of 0.2s at -0.75 V vs. MSE and zero current resting pulses of 4.5s applied to Pt electrode in a 2M HNO_3 + 80mM $HTeO_2^+$+ 110mM Bi^{3+} electrolyte solution;
Figure 5	a) Current responses of every 1000th potential pulse applied to a Pt electrode with an active area of 0.196 cm^2 in a 2M HNO_3 + 80 mM $HTeO_2^+$ + 93 mM Bi^{3+} plating solution, deposition pulses: -0.72 V vs. MSE and 0.2 s, resting pulses: 0 A and 4.5 s. b) Optical microscope image of a polished cross section of the so deposited $Bi_{2+x}Te_{3-x}$;
Figure 6	XRD diffractogram of electrochemically deposited $Bi_{2+x}Te_{3-x}$. Samples (a) and (b) were formed by 50'000 deposition pulses of 80ms at -0.80V vs. MSE and zero current resting pulses of 4.5s onto Pt electrodes immersed in electrolyte containing 2M HNO_3 + 80 mM $HTeO_2^+$ + 93 mM Bi^{3+}. Deposit (a) was measured as deposited with the direction of growth perpendicular to the sample holder plane. Deposit (b) was fine ground to powder before the measurements. The data for the Bi_2Te_3 reference curve and the crystal planes are retrieved from literature;
Figure 7	Atomic ratio of Te/Bi in the deposit vs. the ion concentration of $HTeO_2^+$ to Bi^{3+} in the electrolyte. The concentration of $HTeO_2^+$ was 80mM. Samples are deposited with potential pulses of 100ms at -0.66V vs. MSE and resting pulses of 4.5s with 0A;
Figure 8	Back scattering SEM images of cross section profiles of $Bi_{2+x}Te_{3-x}$ samples deposited under varying potentials. The deposits were each formed with a deposition pulse length of 0.1 s and a resting pulse length of 4.5 s at current of 0A in 2M HNO_3 + 80 mM $HTeO_2^+$ + 80 mM Bi^{3+} electrolyte. The cathodic deposition potential was increased from a) - 0.53V to f) -0.72V vs. MSE;
Figure 9	Atomic ratio of Te/Bi of deposits and deposition rate over deposition potential for samples electroplated with 100ms pulses in 2M HNO_3 + 80 mM $HTeO_2^+$ + 80 mM Bi^{3+} electrolyte as shown in Fig. 8;
Figure 10	Back scattering SEM images of cross sections of electrochemically deposited $Bi_{2+x}Te_{3-x}$ layers deposited with different pulse lengths. The deposits were formed with pulses at -0.66V on Pt in 2M HNO_3 + 80 mM $HTeO_2^+$ + 100 mM Bi^{3+} electrolyte. The resting pulse length was 4.5s at 0A;
Figure 11	SEM image and EDX measurement of sample cross section deposited with the mixed method. The deposit had been formed with potential pulses of 10ms at -0.66V vs. MSE and zero current resting pulse of 4.5s on a Pt electrode in 2M HNO_3 +80mM $HTeO_2^+$ + 60mM Bi^{3+} electrolyte solution. Atomic content of Te and Bi are given according to EDX line scan along dashed dark line;
Figure 12	SEM image of $Bi_{2+x}Te_{3-x}$ thermolegs deposited with the mixed method into a polymer mold that had been structured by photolithography. The mold was removed for demonstration purpose; and
Figure 13	schematically shows a device for electrochemical deposition of chemical compounds and alloys with controlled stoichiometry and/or composition.
Figure 14	schematic representation of the behaviour of the current as a function of time (upper part) and the voltage as a function of time (lower part) in the two basic time intervals t_A and t_B; and
Figure 15	schematically shows a second device for electrochemical deposition of chemical compounds and alloys with controlled stoichiometry and/or composition with a controllable resistance element between the working electrode and the counter electrode.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0050] In the following reference is made to the drawings and figures. These and the following discussion are for the purpose of illustrating the present preferred embodiments of the invention and not for the purpose of limiting the same.

[0051] In this disclosure cyclic voltammetry, chronoamperometry and chronopotentiometry are reported to determine the electrochemical $Bi_{2+x}Te_{3-x}$ formation on Pt electrodes from electrolyte solution with an $HTeO_3^+$ concentration 5 times higher then reported before. Based on these measurements, a new mixed method is introduced that allows full stoichiometric control throughout the entire deposition and that is appropriate to deposit very thick layers (up to 1mm) at a high deposition rate that are free of stress. The influence of the deposition pulse duration, pulse height and electrolyte composition on the stoichiometry and morphology of the $Bi_{2+x}Te_{3-x}$ is disclosed. The feasibility of the proposed method for fabrication of p-and n-type $Bi_{2+x}Te_{3-x}$ is demonstrated by measurements of composition profiles and Seebeck coefficients of the deposits.

[0052] The proposed new method can however equally be applied to the optimisation of existing electrochemical (galvanic) processes, and it may be used to substitute alternative deposition processes for the generation of corresponding layers and devices. Examples are for example the making of thermoelectric coolers and generators on the basis of $Bi_{2+x}Te_{3-x}$, the deposition of CuInSe, CuSe, ZnHgSe, PbCd or CdTe for applications in the field of solar cells, the making of magnetic layers of CiNiFe or CoFe for magnetic datastorage, etc.

[0053] EXPERIMENTAL: All solutions were prepared with DI-water with a resistance >15 MΩcm. The electrolyte solutions were made by dissolving 80 mM TeO_2 (purum, Fluka) and the appropriate amount of BiO_3 (purum, Fluka) in 2 M HNO_3 (65%, puriss, Fluka). This results in a 2 M HNO_3 solution containing Bi^{3+} ions + 80 mM $HTeO_2{}^+$ions.

[0054] All electrochemical experiments were performed with a three electrode configuration, where a Mercury Sulfate Electrode (MSE) was used as reference electrode. This electrode was connected over a salt bridge consisting of 400 mM Na_2SO_4 to the electrolyte solution. A Pt grid was used as counter electrode. The working electrodes were made of n-doped Si chips (Prolog Semicor Ltd.) with evaporated layers of 5nm Cr, 200nm Au and 40nm Pt. For the cyclic voltammetry experiments, the silicon chips were mounted in a PTFE support, which contacts the chip on the metal side. This sample holder exposed a circular area of $28mm^2$ of the chip to the electrolyte. For the electrochemical deposition of $Bi_{2+x}Te_{3-x}$ the exposed area was reduced to $4mm^2$ by a polymer mold. Granting convection during the $Bi_{2+x}Te_{3-x}$ pulse plating, the electrolyte was agitated by a mechanical stirrer. The electrodes were connected to a potentiostate/galvanostate (PGSTAT302, Autolab®) which was computer controlled. The Bi:Te ratios of the deposited layers were analyzed by electron microprobe analysis with a Energy Dispersive X-ray detector (EDX). The Microprobe system was a FEI Quanta 200 FEG Environmental SEM with a Schottky type emitter as electron source. The acceleration voltage was 20kV with 51.2μs amplification time, 100s life time, 33% dead time and a working distance of 10mm. The conversion from intensity counts to element concentration was performed by software provided by the FEI Company.

[0055] For the preparation of samples for cross section and surface analysis the deposits were embedded into a bakelite matrix. The curing of the bakelite powder was performed in a Struers LaboPress-3 under a pressure of 20kN while heated up to 180°C for 6min. The samples were polished with SiC polishing papers under water and an Al_2O_3 suspension with particles size 0.05um on a Struers RotoPol21.

[0056] The crystal structures and crystal orientations were measured by X-ray Diffraction (XRD). The measurement apparatus was a Siemens Kristalloflex & Diffraktometer D5000. The x-ray source was a Cu-Kα tube (wavelength 0.154059 nm), I= 30mA, V=40kV. The measurements parameters were the following: 2 Theta = [5.00; 90.00]°, step size 0.02°, time/step 12.00°, delay time 0.0s, steps 4251, and synchronous rotation on.

[0057] CYCLIC VOLTAMMETRY OF THE SYSTEM Bi AND Te ON Pt: To determine the electrode reactions of the system, cyclic voltammetry (CV) was performed. Figure 1 shows cyclic voltammograms of a Pt electrode recorded in 2M HNO_3 + 80 mM $HTeO_2{}^+$ + 40 mM Bi^{3+} (dashed line), 60 mM Bi^{3+} (solid line), 90 mM Bi^{3+} (doted line) and 110 mM Bi^{3+} (dash doted line). Starting from 0 V, the potential was swept in negative direction to -1V and back to 0.3 V with a scan speed of 10 mV/s. Between -0.4 V and ca. -0.7 V a shoulder D1 at ca. -0.45 V and two peaks D2 and D3 are observed with peak potentials of -0.48 V and -0.55 V respectively. These features are assigned to the Bi and the Te deposition.

[0058] The small shoulder D1 is related to Te deposition on the Pt surface as predicted but not observed by voltammetry.
D1:

$$HTeO_2^{\ +} + 3H^+ + 4e^- \longrightarrow Te + 2H_2O \qquad (1)$$

[0059] Peak D2 is assigned to the Bi_2Te_3 deposition.
D2:

$$3HTeO_2^{\ +} + 2Bi^{3+} + 9H^+ + 18e^- \longrightarrow Bi_2Te_3 + 6H_2O \qquad (2)$$

[0060] Alternatively some bismuth ions might be directly reduced in a reaction with the Te atoms at the electrode surface to form Bi_2Te_3.
D2':

$$3Te + 2Bi^{3+} + 6e^- \longrightarrow Bi_2Te_3 \qquad (3)$$

[0061] However, if there is an excess of $HTeO_2^+$ ions in the electrolyte, i.e. the concentration is larger than necessary to form stoichiometric correct Bi_2Te_3, surplus Te is additionally deposited according to equation (1).

[0062] Peak D3 is observed for concentrations of Bi^{3+} higher than 60mM and further increases with a rise in the Bi^{3+} concentration. Hence D3 may be attributed to the deposition of surplus Bi.
D3:

$$Bi^{3+} + 3e^- \longrightarrow Bi \quad (4)$$

[0063] This reaction occurs only if the ratio of the ion concentrations of Bi^{3+} and $HTeO_3^+$ exceeds the ratio which is necessary for the formation of stoichiometric correct Bi_2Te. In case of this combined Bi and Bi_2Te_3 deposition, the deposition peaks are slightly superposed with the H_2 evolution (reaction 5), which starts to dominate from -0.8 V.

$$2H^+ + 2e^- \longrightarrow H_2 \quad (5)$$

[0064] Since the H_2 evolution is shifted towards more negative potential for decreasing Bi^{3+} concentration, it can be assumed, that the surplus Bi on the surface, which was deposited at peak D3, promotes the formation of H2.

[0065] During the backward scan a broad oxidation peak (O1) between -0.38 V and -0.08 V occurs. This peak decreases with decreasing Bi concentration. This peak is assigned to the oxidation of surplus Bi atoms from a Bi rich $Bi_{2+x}Te_{3-x}$ deposit (reverse reaction of reaction (4)). The broadness of the peak is probably due to slow Bi atom diffusion of the surplus Bi in the Bi_2Te_3 lattice to the electrode interface. Peak O1 ends at the beginning of the double peak (02 and 03). The peak potentials of those peaks are 0.05 V and 0.09 V respectively. We assume that Peak 02 is related to the Bi_2Te_3 stripping (reaction 6) and peak 03 to the stripping of Te that had been deposited at peak D1.
O2:

$$Bi_2Te_3 + 6H_2O \longrightarrow 2Bi^{3+} + 3HTeO_2^+ + 9H^+ + 18e^- \qquad (6)$$

[0066] CHRONOAMPEROMETRIC INVESTIGATIONS OF THE SYSTEM Bi AND Te ON Pt: For the investigation of voltage controlled pulse deposition of $Bi_{2+x}Te_{3-x}$, chronoamperometric measurements have been made. Figure a) shows the pulse form of the applied voltage pulses and b-d) the current response to a series of such potential pulses applied to a Pt electrode in 2 M HNO_3 + 80 mM $HTeO_2^+$ + 110 mM Bi^{3+}. The more cathodic pulses resulting in a negative current response (deposition pulses, deposition intervals) have pulse heights of -0.72 V, and pulse lengths of 1 s. Considering the CV in Figure 1, the deposition pulse is situated more negative to the Bi deposition peak, where a combined Bi and Te deposition resulting in $Bi_{2+x}Te_{3-x}$ formation at a high deposition rate is expected. To set the deposition pulse only to the Bi_2Te_3 deposition peak D2 would not lead to the formation of Bi doped (p-doped) Bi_2Te_3 deposit and would decrease the deposition rate.

[0067] Except for the first deposition pulse, the current response of these pulses all have the same heights and the same current decreases (see Fig. 2c). The first current response looks different because the combined Bi and Te deposition takes place directly on the Pt surface, while in all subsequent pulses the deposition takes place on previously formed $Bi_{2+x}Te_{3-x}$ layers.

[0068] The more positive pulses resulting in a positive current response ("resting pulse"), have pulse heights of -0.25 V and pulse length of 20 s. The current response depicted in Fig.2b) at first sight looks as expected, showing a short but large positive current, indicating the discharge of the double layer, that then drops to zero current. The enlargement of these resting pulses displayed in Fig.2d) gives a different perspective. It can be seen, that the height of the current response continuously increases from the first to the last pulse, and even after 20 s the current does not decrease to zero. Potential pulse plating of Bi and Te resulted in the formation of porous black deposits. It was not possible to form thick stable layers with this method.

[0069] The chronoamperometric results are interpreted as follows: the resting pulse at -0.25 V is situated at the oxidation of the surplus Bi (Fig. 1, peak O1). During the resting pulse after the deposition of $Bi_{2+x}Te_{3-x}$ at -0.72V, surplus

Bi diffuses slowly thought the Bi_2Te_3 matrix to the interface and oxidize there to Bi^{3+}. This leads to an elevated concentration of the surrounding electrode area with Bi^{3+} ions, which results in an increase of Bi deposition in the next deposition pulse. As a result, more surplus Bi is deposited and the Bi oxidation current increases. This increase is relatively hard to observe because the oxidation current is superimposed with the discharging current of the diffusion layer. These effects are increasing with each additional pulse cycle and result in the porous, non stable deposit on the surface. However, setting the potential of the resting pulse to -0.3 V, results in a negative current response. This indicates that at this potential, deposition of Te or Bi_2Te_3 takes place, even though this potential is in the Bi oxidation region O1 of the CV, shown in Fig 1. In general we were not able to find a resting voltage at which the current would drop to 0A. This result will be discussed in the next section.

[0070] CHRONOPOTENTIOMETRIC INVESTIGATIONS OF THE SYSTEM Bi AND Te ON Pt: In this section, chronopotentiometric measurements which were performed to investigate the properties of $Bi_{2+x}Te_{3-x}$ plating by current pulses are described. Figure a) shows the current pulse sequence that alternates between deposition pulses with pulse heights of -0.04 A and pulse length of 1 s and resting pulses at 0 A with a pulse length of 20 s. The recorded potential response to a series of such current pulses applied to a Pt electrode in 2 M HNO_3 + 80 mM $HTeO_2^+$ + 110 mM Bi^{3+} is shown in Fig. 3b)-d). The potential responses to the -0.04 A deposition pulses show, in the beginning of the pulse, a shoulder between -0.6 V and -0.7 V. After the shoulder, a strong negative potential increase can be observed as can be seen in Fig. 3b). The height of the increase varies from pulse to pulse. The potential shoulder can be related to $Bi_{2+x}Te_{3-x}$ deposition. This deposition decreases the Bi^{3+} and $HTeO_2^+$ ion concentration of the surrounding area of the working electrode. To hold the current constant, the potential is increased, into the N_2 evolution (strong potential increase after the shoulder). The voltage response at the deposition shoulder shows a slope of about 125mV/s in the range between 0.1-0.7s (see Fig.3c)), which is also caused by the onset of the depletion of ions. A potential shift of 50-100mV is expected to cause a significant change in the stoichiometry of the deposit according to reported results on potentiostatic deposition. Reducing the duration of the deposition pulse to 1-10 ms would certainly limit the potential shift but for deposition of thick layers >500μm the electrical resistance and the surface area of the deposit will increase causing again a potential shift, that will influence the controlled $Bi_{2+x}Te_{3-x}$ deposition.

[0071] Figure d) shows an enlargement of the potential response during the resting pulses at 0 A. It can be observed, that the potential does not remain constant and that for each pulse the potential decreases to a different value. Considering this potential range in the backward scan of the CV in Figure 1, it can be observed that the potential shifts from the Te and Bi_2Te_3 deposition at peaks D1 and D2 into the Bi oxidation peak O1. Two possible explanations for this phenomenon can be assumed. (1) The $Bi_{2+x}Te_{3-x}$ electrode is at the equilibrium potential, which is unstable and shifts vs. more positive potentials. (2) A superposition between deposition of Te and oxidation of previous deposited surplus Bi takes place at potentials between ca. 0.38 V and ca. 0.26V. By applying zero current after a deposition pulse, to the working electrode, the amount of electrons used for the $HTeO_2^+$ reduction has to be equal to the amount electrons gained by the oxidation of surplus Bi as shown in the following redox equation.

$$3HTeO_2^+ + 3H^+ + 4Bi \longleftrightarrow Te + 4Bi^{3+} + 3H_2O \qquad (5)$$

[0072] Since, the Bi oxidation and Te deposition are related to each other during a zero current pulse following a deposition pulse; the decrease of the Bi concentration in the Bi_2Te_3 matrix, would lead to a reduced use of Te, which is balanced by the observed positive potential shift. Hence, the resting potential is quasi self adjusted by the described equilibrating reaction. This also explains why it was impossible to find a fixed resting potential during chronoamperometric experiments.

[0073] CONCLUSION OF THE FIRST PART: Chronoamperometric and chronopotentiometric measurements show that neither potential pulse deposition (voltage control) nor current pulse deposition (current control) can lead to a controlled and stable deposition of $Bi_{2+x}Te_{3-x}$.

[0074] It is therefore according to the invention proposed to combine voltage controlled deposition pulses, for repetitive and exact control of reduction reactions, with current controlled resting pulses that allow undisturbed equilibrating reactions between deposit and ions at the electrode-electrolyte interface. By applying this "mixed method" one achieves precisely controllable deposition of thick layers of $Bi_{2+x}Te_{3-x}$ with a homogeneous and defined stoichiometry, which are suitable for fabrication of p- and n-type thermolegs.

[0075] CONTROLLED ELECTRODEPOSITION OF $Bi_{2+x}Te_{3-x}$ WITH THE MIXED METHOD, A COMBINATION OF POTENTIAL DEPOSITION PULSES AND ZERO CURRENT RESTING PULSES TOWARDS N- AND P-DOPED $Bi_{2+x}Te_{3-x}$: Here the new method for the formation of thick $Bi_{2+x}Te_{3-x}$ layers is presented. To show the feasibility of this method, voltammetric stripping experiments were performed on $Bi_{2+x}Te_{3-x}$ layers, which had been deposited with the mixed method according to the invention. Figure shows linear sweep voltammograms recorded in 2M HNO_3 of a Pt electrode with a $Bi_{2+x}Te_{3-x}$ deposit on top.

[0076] This $Bi_{2+x}Te_{3-x}$ was previously deposited in a 2M HNO_3 + 80mM $HTeO_2^+$+ 110mM Bi^{2+} electrolyte solution by 1, 4 and 16 pulses of 0.2s with a deposition pulse height - 0.75 V and zero current resting pulses of 4.5s.

[0077] After the deposition, the electrodes were cleaned in 2M HNO_3 and then transferred to 2M HNO_3 electrolyte solution, where the potential was swept from -0.7V to 0.3V with a scan speed of 10mV/s. During this scan, one oxidation peak (02) was observed, which increases with the number of deposition pulses due to higher amount of deposited Bi_2Te_3. In comparison to the cyclic voltammograms shown in Figure 4, peak O1 and 03 are missing, which indicates that primarily Bi_2Te_3 is produced with this method. The absence of peak 03 in Figure additionally proves, that 03 is indeed related to the oxidation of a small layer of Te, which is produced only during potential sweep deposition but not with pulse deposition.

[0078] PROCESS AND SETUP OPTIMIZATION BY DEPOSITION PULSE MONITORING: It is possible to record the current response of any potential pulses. Thereby, the processes at the electrode surface can be monitored and analyzed. This procedure provides substantial assistance for the optimization of the experimental setup and the deposition process.

[0079] For example, the undesired formation of H_2 bubbles on the working electrode is indicated by a drop of the recorded current response, which is due to the decrease of the electrode surface caused by the bubble. On the other hand, stress induced cracking or bursting of the deposit is indicated by a sudden increase in the current, because of an increase in electrode surface area. Furthermore, convection conditions may be optimized by analysis of the current responses. The results of the process optimization enabled the deposition of thick layers of $Bi_{2+x}Te_{3-x}$.

[0080] Figure a) shows the current response of every 1000th potential pulse recorded during the plating of the $Bi_{2+x}Te_{3-x}$ layer shown in microscope image in Fig. 5b).

[0081] The deposition was carried out with potential pulses of 0.2s at -0.72 V (deposition pulses, voltage controlled) and resting pulses of 4.5s with 0A on a sandblasted Pt electrode in a 2M HNO_3 + 80 mM $HTeO_2^+$ + 93 mM Bi^{3+} electrolyte solution.

[0082] The overall current rises with increasing pulse number because of the increase in surface roughness and hence in surface area of the electrode. Undisturbed growth of a thick $Bi_{2+x}Te_{3-x}$ layer was achieved because formation of H_2 bubbles on the electrode surface was avoided by a setup with vertical orientation of the working electrode and elevated mechanical convection. The 12000 deposition pulses resulted in a $Bi_{2+x}Te_{3-x}$ thickness of 780 ± 50 μm yielding a deposition rate of 50 μm/h.

[0083] CONTROL OF STOICHIOMETRY AND MORPHOLOGY OF THE $Bi_{2+x}Te_{3-x}$ DEPOSIT: The dependency of the deposits' stoichiometry and morphology from deposition potential, concentration of Bi^{3+} ions in the electrolyte and deposition pulse duration was investigated in a series of experiments. The deposition pulses were applied to Pt working electrodes in a 2 M HNO_3 + 80mM $HTeO_2^+$ + Bi^{3+}. The Bi^{3+} concentration was varied form 110 mM to 40 mM. The potential pulse heights and the deposition pulse durations were varied in the ranges between -0.72 V and -0.53 V and 10 ms and 200 ms, respectively. The duration of the 0 A resting pulses, was 4.5 s. The samples were deposited to a minimum thickness of 200μm. For preparation, the deposits are removed from the substrate, embedded in epoxy and polished. The EDX measurements were performed along the polished cross section profile of each sample to determine the ratio of Te and Bi atoms throughout the deposit. SEM pictures were taken of profiles or sample surfaces to evaluate the morphology of the deposit.

[0084] INFLUENCE OF ELECTROLYTE COMPOSITION: In order to determine the influence of the electrolyte composition on the stoichiometry several depositions in electrolytes varying in concentration of Bi^{3+} ions but with a constant concentration of 80 mM $HTeO_2^+$ were carried out. The deposition potential and the deposition pulse duration were set to -0.66V and 0.1s, respectively. Figure 7 shows the results of the EDX measurements which were performed on the cross section profile of each sample. Each point represents the average value of 128 measuring points, which were evenly distributed on a line on the profile that is parallel to direction of growth. The error bars are equivalent to the standard deviation of these measuring points.

[0085] The atomic ratio of tellurium to bismuth in the deposit is proportional to the ratio of the concentration of $HTeO_2^+$ to Bi^{3+} ions in the electrolyte and may therefore be adjusted by this electrolyte concentration ratio. The slope of the linear fit in Figure 7 has a value of 1.15. This result is comparable to literature for lower concentrated electrolytes, and indicates that the concentration of Bi ions in the electrolyte needs to be above the desired stoichiometry in the deposit.

[0086] Stoichiometric Bi_2Te_3 may be deposited with an ionic ratio of 1.31 $HTeO_2^+$ to Bi^{3+} ions. Subsequently, ratios above and below this value will yield Te rich and Bi rich deposits respectively. According to literature $Bi_{2+x}Te_{3-x}$ which is Te rich ($x<0$) should exhibit a n-type behavior, i.e. posses a negative Seebeck coefficient, whereas Bi rich ($x>0$) material should show p-type behaviour.

[0087] INFLUENCE OF THE DEPOSITION POTENTIAL: In a series of experiments, the influence of the deposition potential on the morphology and stoichiometry of the deposit were investigated. The samples were electrochemically deposited with the mixed method in 2 M HNO_3 + 80mM $HTeO_2^+$ + 80mM Bi^{3+} and with deposition pulse duration of 100ms.

[0088] The influence of the deposition potential on the morphology of the deposit is illustrated by means of the backscattering SEM images of polished cross section profiles shown in Figure 8. For low potentials from a) -0.53V to b) -0.57 V a very compact and uniform deposit is formed. No grain boundaries are visible but the layer exposes cracks caused by stress which additionally leads to poor adhesion. For samples deposited at more cathodic potentials (samples c) to f)) the stress-induced cracks disappear, grain boundaries become visible and the roughness of the profile increases when shifting the deposition potentials towards more negative values. In the initial 5 to 10 μm of the layer the grain size is quite small (< 1μm). Then, larger grains of up to 50 μm evolve which arrange along the direction of growth. Samples c) and d) deposited at -0.63 and -0.66V vs. MSE, respectively, show a compact structure with large column like grains. For higher potentials e) -0.69V and f) -0.72V, more dendrite-like grains evolves and voids in increasing number and size appear.

[0089] The variation in morphology can be explained by the rate of deposition, which is shown in Figure 9 . As expected, the deposition rate rises with the magnitude of the deposition potential. Dendrite like growth, increased surface roughness and appearance of voids are promoted by fast deposition rates as for samples f) and e). As a result, a larger stochastic derivation in the atomic composition of the deposits, reflected by larger error bar in the EDX measurement data in Figure 9, is noted.

[0090] A range of deposition potentials from -0.63 to -0.66V vs. MSE seems most suitable for fabrication because it yields homogenous, compact and low stress deposits at deposition rates of about 50μm/h.

[0091] Figure 9 also depicts the influence of the deposition potential on the composition of the deposit. For the potential range between -0.72V and -0.63V, the atomic ratio of tellurium to bismuth in the deposit stays constant at a value of 1.2. This behavior may be explained by means of the cyclic voltamogramm in Figure 1. The deposits are bismuth rich because they have been formed at potential more negative than the two reduction peaks, D2 and D3, of the system. Hence, additional Bi is incorporated in the bismuth telluride crystal. For more positive potentials, the ratio increases to 1.4 for -0.57 V, to a nearly stoichiometric composition of 1.48 for the sample deposited at -0.53 V. At these potentials, the additional Bi deposition according to equation (4) at peak D3 in the CV is very low, hence, primarily stoichiometric Bi_2Te_3 is deposited. The results of the composition measurement support the assignment of the reduction peaks in the CV and confirm the importance of potential control during deposition in order to avoid composition variations and stress problems.

[0092] It is also possible to adjust the deposits stoichiometry by means of the deposition potential. However for practical reasons, i.e. maintaining a high deposition rate and stress free deposits, it is recommended to rather adjust it with ionic concentration ratio as described before.

[0093] INFLUENCE OF DEPOSITION PULSE DURATION: The influence of the deposition pulse length on morphology and stoichiometry was investigated by additional experiments. The examined samples were prepared with deposition pulses of varying duration while the duration of the zero current resting pulse was set to 4.5 seconds. All sample were deposited at -0.66V in 2 M HNO_3 + 80mM $HTeO_2^+$ + 100mM Bi^{3+}.

[0094] The pulse duration mainly influences the morphology of the deposit as can be seen in Figure showing back scattering SEM images of the sample cross sections. With increasing pulse length the grain size, the number and size of voids increases, the surface roughness increases, and the deposit becomes less compact. The stoichiometry does not vary significantly with the pulse duration.

[0095] For 10ms pulses, the deposition yields a very compact deposit but several cracks indicate an increased level of stress in the layer. For the determination of the optimal pulse duration, the area to be plated needs to be considered. The plating of large cohesive areas is much more vulnerable to layer stress than plating into small holes. The bigger the ratio of circumference to surface of an area to be plated the more boundaries there will be for stress release and the better the adhesion will be. Additionally, the sidewalls of a mold provide stability to the deposit. Application of short pulses may be beneficial, if not necessary, for ECD into high aspect ratio molds.

[0096] VARIATION OF STOICHIOMETRY OVER THICKNESS: Composition measurements along profiles of electrochemically deposited bismuth telluride reveal variations in the composition that cause the formation of a p-n junction within the deposited layer. As a result, unwanted thermoelectric behaviour, i.e. a negative Seebeck coefficient in a Bi-rich deposit, is observed. In order to achieve the desired thermoelectric properties, a constant composition profile may be necessary.

[0097] The variation of the stoichiometric composition over the thickness of various samples fabricated with the mixed method was investigated by EDX measurements across polished cross section profiles. Figure 11 shows the secondary electron SEM image and the results of an EDX measurement across the profile of a sample deposited with potential pulses of 10ms at -0.66V vs. MSE on a Pt electrode in a 2 M HNO_3 + 80mM $HTeO_2^+$ + 60mM Bi^{3+} electrolyte solution at a rate of 20μm/h.

[0098] The sample exhibits a very constant composition over its entire thickness. The atomic ratio of Te to Bi is 1.50±0.06. Hence, stoichiometric Bi_2Te_3 has been deposited. For all samples deposited with pulses of 10ms and shorter, the variation of the composition was below 0.1

[0099] The demonstrated deposition with constant stoichiometry is a requirement for the specific control and optimization of the thermoelectric properties of electroplated $Bi_{2+x}Te_{3-x}$.

[0100] MEASUREMENT OF SEEBECK COEFFICIENT: In order to prove the suitability of the proposed method for fabrication of both p- and n-type $Bi_{2+x}Te_{3-x}$, first measurements of the Seebeck coefficient have been performed. The measurements were performed across the thickness of the deposits, which had not been annealed.

[0101] The Bi-rich samples with Te content below 60% show a positive Seebeck coefficient with a maximum value of 55μV/K. The Te rich deposits with Te content higher than 60% exhibit a negative Seebeck coefficient of -40μV/K.

[0102] Until now, only measurement of undoped n-type $Bi_{2+x}Te_{3-x}$ has been reported. With the presented invention, the feasibility of fabrication of undoped p-type $Bi_{2+x}Te_{3-x}$ by means of electrochemical deposition has been demonstrated for the first time. This is the result of the enhanced uniformity of composition achieved for deposits fabricated with the introduced method.

[0103] CONCLUSION: A comprehensive electrochemical investigation of the system Bi and Te on Pt in 2M HNO_3 including cyclic voltammetry, chronoamperometry and chronopotentiometry demonstrates the new mixed method for the electrochemical deposition of $Bi_{2+x}Te_{3-x}$, which combines voltage controlled deposition pulses with current controlled resting pulses. The stoichiometry of the deposits can be controlled to be constant over the thickness and may be adjusted by the ratio of ionic concentration in the electrolyte and the potential of the deposition pulse. The method allows stable and stress free deposition of very thick layers of Bi Te at high rate. Sample thicknesses of >800μm and deposition rates of up to 73μm/h have been achieved exceeding the values previously reported by a factor of 2.3 and 3.6 respectively. The high deposition rates could be achieved by deposition at low pH values with ionic concentrations of Bi and Te ions 4-5 times higher than reported in literature. The fabrication of n- and p-type $Bi_{2+x}Te_{3-x}$ was successfully verified by Seebeck measurements. The presented technology may be incorporated into the process flow for low cost fabrication of flexible micro thermoelectric devices made of $Bi_{2+x}Te_{3-x}$ thermolegs as shown in Figure 12. The proposed method can also be applied for electrochemical deposition of other binary or ternary or generally multinary compounds.

[0104] DEVICE: Figure 13 shows a device for electrochemical deposition of chemical compounds and alloys with controlled stoichiometry and/or composition. The electrolyte 1 is provided in the corresponding container, and at least two, preferably three electrodes are located in the electrolyte bath.

[0105] On the one hand there are one or more working electrodes WE to which one or more devices to be coated are connected. On the other hand there are one or more counter electrodes CE and optionally one or more reference electrodes RE and/or additional electrodes. The device thus allows connection of several groups of WE, CE and optional RE for simultaneous deposition on multiple workpieces.

[0106] The potentials and currents at the electrodes are monitored and/or controlled by means of a voltmeter 2 and an amperemetre 3, respectively.

[0107] The potential applied or measured between WE and RE or CE is controlled and governed by the power supply and mixed method control unit 4. Unit 4 additionally controls and governs and/or measures the current flow between WE and CE..

[0108] It should be noted that presently available control units for ECD can either be operated in exclusively current controlled mode **or** in exclusively voltage controlled mode. Devices are available which can be operated in both modes, however the two modes have to be selected for a specific cycle and it is not possible to combine the two modes in one ECD-cycle.

[0109] Correspondingly the proposed device for the first time provides the possibility to carry out the proposed method in that it comprises a current source element 8 which allows to provide the two electrodes WE and CE with a precisely controlled current of desired value. On the other hand it comprises a voltage source 9 element, which allows to provide the two electrodes WE and CE with a precisely controlled potential or voltage of desired value.

[0110] Furthermore it comprises an open circuit pathway 7 and a short-circuit pathway 6, which also allow control over the desired current and/or potential applied.

[0111] The units 6-9 can independently be switched on or off and therefore connected to the two electrodes WE and CE by means of one ore more triggered switches 5.

[0112] It is for example possible to operate the device in the case of zero current relaxation period and voltage controlled deposition period by switching with the triggered switches 5 between the elements 7 (current controlled period) and 9 (potential controlled period). Correspondingly the switching time of one or more triggered switches should be in the nanosecond to low millisecond or to low microsecond range in order to allow fast switching of the pulses. The triggered switches are synchronously clocked for the generation of the pulse sequence.

[0113] In figure 14 in the upper part the current as effective between the working electrode and the counter electrode is shown as a function of time for the two basic intervals t_A and t_B. In the lower part the voltage as effective between the reference electrode and the working electrode is shown as a function of time for the two basic time intervals. Generally solid lines indicate adjusted i.e. specifically controlled parameters while dashed lines indicate parameters which are self adjusting.

[0114] As one can see in the first time interval t_A the deposition is controlled such that between the reference electrode and the working electrode a constant voltage (15a) is maintained. This means that the working electrode is kept at a constant voltage level (15a) with respect to the reference electrode and therefore to the electrolyte. One can therefore say that the working electrode is kept at a constant voltage on absolute level. In the meantime the current flowing between the working electrode and the counter electrode (as indicated with reference 14a), depending on the deposition processes and other processes around the electrodes and in the electrolyte taking place on the working electrode, is changing as a function of time.

[0115] Switching to the second time interval t_B now the current flowing between the working electrode and the counter electrode is maintained and controlled to be at a constant level (14b). In the meantime the voltage between the reference electrode and the working electrode, again depending on the deposition processes taking place on the working electrode and other processes around the electrodes and in the electrolyte, is changing as a function of time, very often showing an asymptotic behaviour as illustrated in figure 14 with reference 15b. As typically the resistance between the reference electrode and the working electrode is essentially infinitely high, no current is flowing between the reference electrode and the working electrode.

[0116] Figure 15 shows addition to the device as described above for carrying out the method according to the invention, the elements of this device may however also be combined with the one as illustrated in figure 13. The device is adapted to the deposition of chemical compounds and alloys with controlled morphology. In this case a variable resistance 11 is provided between the working electrode WE and the counter electrode CE. The variable resistance 11 can be realised alternatively as illustrated on the right-hand side of figure 15. It may either be realised by providing an automatically controllable resistance 12 which is controlled by a controller 10 (upper part). The control variable for controller 10 is the amperemetre illustrated with A in the figure. Correspondingly therefore depending on the current measured in the pathway between the working electrode WE and the counter electrode CE the resistance 12 is tuned in order to keep the current during interval t_B at a desired level.

[0117] In the alternative (or in addition to that for the generation of an offset), as illustrated in the lower part on the right-hand side of figure 15, it is possible to have a manually controlled variable resistance 13.

LIST OF REFERENCE NUMERALS

[0118]

1	electrolyte
2	voltmeter
3	amperemetre
4	power supply and mixed method control unit
5	triggered switch, e.g. mechanical, electromechanical, IC or electrical
6	short-circuit
7	open circuit
8	current source
9	voltage source
10	controller
11	variable resistance element
12	variable resistor (automatically controllable)
13	variable resistor (manual)
14	current as a function of time during the two basic intervals
14a	variable current behaviour during ta
14b	constant current behaviour during tb
15	voltage as a function of time during the two basic intervals
15a	constant voltage behaviour during ta
15b	variable current behaviour during tb
RE	reference or additional electrode
WE	working electrode
CE	counter electrode

Claims

1. Method for depositing an alloy and/or chemical compounds on a substrate immersed in a liquid electrolyte (1), comprising the steps of:

   I. applying a first constant or varying potential to the substrate under voltage control for a deposition time interval (tA);
   II. applying a second constant or varying current to the substrate under current control for a relaxation time interval (tB);

repeating the sequence of steps I-II at least twice.

2. Method according to claim 1, wherein a reference electrode (RE) or a pseudo-reference electrode, a working electrode (WE) and a counter electrode (CE) are immersed in the liquid electrolyte (1), and wherein
during step 1. the potential is controlled to be constant, or controlled to be variable according to a predefined time dependency of the potential, between the reference electrode (RE) or pseudo-reference electrode and the working electrode (WE) keeping the working electrode (WE) at an absolutely controlled voltage level with respect to the electrolyte (1), while the potential between the working electrode (WE) and the counter electrode (CE) is allowed to vary and adapt as a function of time, and wherein
during step II. the current is controlled to be constant, or controlled to be variable according to a predefined time dependency of the current, between the working electrode (WE) and the counter electrode (CE), while the voltage between reference electrode (RE) and the working electrode (WE) is allowed to vary as a function of time and adapt to this situation while not becoming zero.

3. Method according to any of claims 1 or 2, the current flowing between the working electrode and the counter electrode is controllably reduced in particular during step I, while the potential between the working electrode and the reference electrode remain unchanged, wherein preferably control in particular during step I takes place using an adaptable and controllable resistance (11) between the working electrode (WE) and the counter electrode (CE), wherein preferably control of this resistance (11) is effected using a feedback loop by current measurement in the path between working electrode (WE) and counter electrode (CE).

4. Method according to any of the preceding claims, wherein during the deposition time interval (tA) the voltage is controlled to be constant, preferably within a tolerance range of at most ±0.1 V, most preferably within a tolerance range of at most ±500 μV.

5. Method according to any of the preceding claims, wherein during the relaxation interval (tB) the current is kept constant, preferably within a tolerance range equivalent to a current density on the substrate of at most ±10mA/cm2, most preferably within a tolerance range of at most ±1 μA/cm2.

6. Method according to any of the preceding claims, wherein during the relaxation interval (tB) the current is at zero, preferably within a tolerance range equivalent to a current density on the substrate of at most ±10mA/cm2, most preferably within a tolerance range of at most ± 1 μA/cm2.

7. Method according to any of the preceding claims, wherein during the deposition time interval (tA) the absolute value of the voltage is above the nucleation potential of the reacting substance, preferably at least 0.1 V or in the range of 0.1 - 3.0V, most preferably in the range of 0.4 - 1.0V.

8. Method according to any of the preceding claims, wherein the deposition time interval (tA) is in the range of 1 μs-60s, preferably in the range of 1 ms-1 s, most preferably in the range of 1-200 ms.

9. Method according to any of the preceding claims, wherein the relaxation time interval (tB) is in the range of 1 μs-60s, preferably in the range of 1 ms-30s, most preferably in the range of 1-5s.

10. Method according to any of the preceding claims, wherein the duty cycle of the deposition time interval (tA) to the relaxation time interval (tB) is below 80%, or below 50%, preferably below 25%, most preferably below 10%.

11. Method according to any of the preceding claims, wherein the stoichiometry of the deposited alloy and/or a chemical compound is controlled by means of at least one correspondingly adapted parameter selected from the following group: value of voltage and/or length (tA, tB) of the deposition and/or relaxation time interval; duty cycle, current density, ionic concentration ratio of the starting materials of the alloy/compound dissolved as ions in the electrolyte (1).

12. Use of a method according to any of the preceding claims for depositing a semiconducting material, a thermoelectric material, or a magnetic material, preferably on the basis of at least one of the materials selected from the following group: Bi2+xTe3-x, CuInSe, BiSbTe, BiSeTe, SbTe, GeTe, AgSe, PbTe, TeAgGeSb, AgSb, SnTe, CuSe, ZnHgSe, PbCd or CdTe, CiNiFe or CoFe onto a substrate.

13. Use according to claim 12 for depositing Bi2+xTe3-x, wherein the voltage during the deposition time interval (tA) is selected in the range (-10.0) - (-0.1)V, preferably (-1.0) - (-0.3)V, and wherein during the relaxation time interval

there is a controlled current of I=0, wherein preferably, for depositing p-type Bi2+xTe3-x, the ratio of [HTe02+] to [Bi3+] in the electrolyte (1) is chosen such that the atomic ratio Te : Be in the deposit is below 1.6,or below 1.5,or below 1.25, and wherein even more preferably the electrolyte solution comprises at least 1.5M HN03, at least 30mM [HTe02+] and/or at least 30mM [Bi3+].

14. Method according to any of the claims 1-11, wherein before the starting any of steps I. and/or II, the liquid electrolyte (1) is prepared by providing a concentrated HNO_3 solution, preferably in a concentration of more than 70 %, heating it up to boiling temperature or until not more than 40° below boiling point, preferably not more than 5° below boiling point, addition of TeO_2 in the desired amount, stirring of the corresponding solution and successive water addition to the solution until essentially complete dissolution of TeO_2, followed by an optional decrease of temperature to below 80°, addition of Bi_2O_3 in the desired amount, stirring until essentially complete dissolution of all constituents, addition of water until reaching a desired HNO_3 concentration, preferably of in the range of 2M.

Patentansprüche

1. Verfahren zum Abscheiden einer Legierung und/oder chemischer Zusammensetzungen auf einem Substrat, das in einen flüssigen Elektrolyten (1) ein getaucht ist, welches die folgenden Schritte umfasst:

I. Anlegen eines ersten konstanten oder variierenden Potenzials an das Substrat unter Spannungskontrolle für ein Abscheidungszeitintervall (tA);
II. Anwenden eines zweiten konstanten oder variierenden Stroms auf das Substrat unter Spannungskontrolle für ein Abscheidungszeitintervall (tB);

Wiederholen der Folge der Schritte I-II mindestens zweimal.

2. Verfahren nach Anspruch 1, wobei eine Referenzelektrode (RE) oder eine Pseudoreferenzelektrode, eine Arbeitselektrode (WE) und eine Gegenelektrode (CE) in den flüssigen Elektrolyten (1) eingetaucht sind, und wobei während Schritt I das Potenzial so gesteuert wird, dass es konstant ist, oder so gesteuert wird, dass es gemäß einer vorgegebenen Zeitabhängigkeit des Potenzials zwischen der Referenzelektrode (RE) oder Pseudoreferenzelektrode und der Arbeitselektrode (WE) variabel ist, wobei die Arbeitselektrode (WE) auf einem absolut kontrollierten Spannungsniveau gegenüber dem Elektrolyten (1) gehalten wird, während das Potenzial zwischen der Arbeitselektrode (WE) und der Gegenelektrode (CE) variieren und sich als Funktion der Zeit anpassen darf, und wobei während Schritt II. der Strom so gesteuert wird, dass er konstant ist, oder so gesteuert wird, dass er gemäß einer vorgegebenen Zeitabhängigkeit des Stroms variabel sein darf, zwischen der Arbeitselektrode (WE) und der Gegenelektrode (CE) variabel sein darf, während die Spannung zwischen der Referenzelektrode (RE) und der Arbeitselektrode (WE) als Funktion der Zeit variieren und sich an diese Situation anpassen darf, dabei aber nicht null wird.

3. Verfahren nach einem der Ansprüche 1 oder 2, wobei der Strom, der zwischen der Arbeitselektrode und der Gegenelektrode fließt, kontrollierbar reduziert wird, insbesondere während Schritt I, während das Potenzial zwischen der Arbeitselektrode und der Referenzelektrode unverändert bleibt, wobei vorzugsweise eine Steuerung insbesondere während Schritt I unter Verwendung eines anpassbaren und steuerbaren Widerstandes (11) zwischen der Arbeitselektrode (WE) und der Gegenelektrode (CE) stattfindet, wobei die Steuerung dieses Widerstandes (11) unter Verwendung einer Rückkopplungsschleife durch Strommessung im Pfad zwischen Arbeitselektrode (WE) und Gegenelektrode (CE) bewirkt wird.

4. Verfahren nach einem der vorherigen Ansprüche, wobei während des Abscheidungszeitintervalls (tA) die Spannung konstant gehalten wird, vorzugsweise innerhalb eines Toleranzbereichs von höchsten ±0,1 V, am besten innerhalb eines Toleranzbereichs von höchstens ±500 µV.

5. Verfahren nach einem der vorherigen Ansprüche, wobei während des Relaxationsintervalls (tB) der Strom konstant gehalten wird, vorzugsweise innerhalb eines Toleranzbereichs, der äquivalent zu einer Stromdichte auf dem Substrat von höchstens ±10 mA/cm2, am besten innerhalb eines Toleranzbereichs von höchstens ±1 µA/cm2 ist.

6. Verfahren nach einem der vorherigen Ansprüche, wobei während des Relaxationsintervalls (tB) der Strom bei null wird, vorzugsweise innerhalb eines Toleranzbereichs, der äquivalent zu einer Stromdichte auf dem Substrat von höchstens ±10 mA/cm^2, am besten innerhalb eines Toleranzbereichs von höchstens ±1 $\mu A/cm^2$ ist.

7. Verfahren nach einem der vorherigen Ansprüche, wobei während des Abscheidungszeitintervalls (tA) der Absolutwert der Spannung oberhalb des Blasenbildungspotenzials der reagierenden Substanz ist, vorzugsweise mindestens 0,1 V oder im Bereich von 0,1 V - 3,0 V, am besten im Bereich von 0,4 V - 1,0 V.

8. Verfahren nach einem der vorherigen Ansprüche, wobei das Abscheidungszeitintervall (tA) im Bereich von 1 µs-60 s, vorzugsweise im Bereich von 1 ms-1 s, am besten im Bereich von 1-200 ms liegt.

9. Verfahren nach einem der vorherigen Ansprüche, wobei das Relaxationszeitintervall (tB) im Bereich von 1 µs-60 s, vorzugsweise im Bereich von 1 ms-30 s, am besten im Bereich von 1-5 s liegt.

10. Verfahren nach einem der vorherigen Ansprüche, wobei das Tastverhältnis des Abscheidungszeitintervalls (tA) zum Relaxationszeitintervall (tB) unter 80 % oder unter 50 %, vorzugsweise unter 25 %, am besten unter 10 % liegt.

11. Verfahren nach einem der vorherigen Ansprüche, wobei die Stöchiometrie der abgeschiedenen Legierung und/oder einer chemischen Verbindung mittels mindestens eines entsprechend angepassten Parameters gesteuert wird, der aus der folgenden Gruppe ausgewählt wird: Wert von Spannung und/oder Länge (tA, tB) des Abscheidungs- und/oder Relaxationszeitintervalls; Tastverhältnis, Stromdichte, ionisches Konzentrationsverhältnis der Startmaterialien der Legierung/Verbindung, die als Ionen im Elektrolyt (1) aufgelöst ist.

12. Verwendung eines Verfahrens nach einem der vorherigen Ansprüche zum Abscheiden eines halbleitenden Materials, eines thermoelektrischen Materials oder eines magnetischen Materials, vorzugsweise auf der Basis von mindestens einem der Materialien, das aus der folgenden Gruppe ausgewählt wird: $Bi_{2+x}Te_{4-x}$, CuInSe, BiSbTe, BiSeTe, SbTe, GeTe, AgSe, PbTe, TeAgGeSb, AgSb, SnTe, CuSe, ZnHgSe, PbCd oder CdTe, CiNiFe oder CoFe, auf einem Substrat.

13. Verwendung nach Anspruch 12 zum Abscheiden von $Bi_{2+x}Te_{4-x}$, wobei die Spannung während des Abscheidungszeitintervalls (tA) im Bereich (-10,0) - (0,1) V, vorzugsweise (-1,0) - (-0,3) V gewählt wird und wobei es während des Relaxationszeitintervalls einen gesteuerten Strom von 1=0 gibt, wobei vorzugsweise das Verhältnis von [$HTeO_2$+] zu [Bi_3+] im Elektrolyten (1) zum Abscheiden von $Bi_{2+x}Te_{3-x}$ vom p-Typ so gewählt wird, dass das Atomverhältnis Te:Be in der Abscheidung unter 1,6 oder unter 1,5 oder unter 1,25 ist und wobei besser die Elektrolytlösung mindestens 1,5 M HNO_3, mindestens 30 mM [$HTeO_2$+] und/oder mindestens 30 mM [Bi_3+] umfasst.

14. Verfahren nach einem der Ansprüche 1-11, wobei vor dem Starten der Schritte I und/oder II der flüssige Elektrolyt (1) vorbereitet wird, indem eine konzentrierte HNO_3-Lösung, vorzugsweise in einer Konzentration von mehr als 70 %, Erwärmen derselben bis zur Siedetemperatur oder bis zu nicht mehr als 40° unter dem Siedepunkt, vorzugsweise nicht mehr als 5° unter dem Siedepunkt, Zusetzen von Te02 in der gewünschten Menge, Rühren der entsprechenden Lösung und fortlaufendes Zusetzen von Wasser zur Lösung bis zur im Wesentlichen vollständigen Auflösung von Te02, gefolgt von einer optionalen Verringerung der Temperatur unter 80°, Zusetzen von Bi_2O_3 in der gewünschten Menge, Rühren bis zur im Wesentlichen vollständigen Auflösung aller Bestandteile, Zusetzen von Wasser bis zum Erreichen einer gewünschten HNO_3-Konzentration, vorzugsweise im Bereich von 2 M, bereitgestellt wird.

Revendications

1. Procédé de dépôt d'un alliage et/ou de composés chimiques sur un substrat immergé dans un électrolyte liquide (1), comprenant les étapes consistant à :

I. appliquer une première constante ou variation de tension sur le substrat sous régulation de tension pendant un intervalle de temps de dépôt (tA) ;
II. appliquer une deuxième constante ou variation de courant sur le substrat sous régulation de tension pendant un intervalle de temps de relaxation (tB) ;

répéter la séquence d'étapes I-II au moins deux fois.

2. Procédé selon la revendication 1, dans lequel une électrode de référence (RE) ou une pseudo-électrode de référence, une électrode de travail (WE) et une contre-électrode (CE) sont immergées dans l'électrolyte liquide (1), et dans lequel,
pendant l'étape I, la tension est régulée de façon à être constante, ou est régulée de façon à varier selon une

dépendance prédéfinie de la tension par rapport au temps, entre l'électrode de référence (RE) ou la pseudo-électrode de référence et l'électrode de travail (WE) maintenant l'électrode de travail (WE) à un niveau de tension absolument régulé par rapport à l'électrolyte (1), tandis que la tension entre l'électrode de travail (WE) et la contre-électrode (CE) peut varier et s'adapter en fonction du temps, et dans lequel
pendant l'étape II, le courant est régulé de façon à être constant, ou est régulé de façon à varier selon une dépendance prédéfinie du courant par rapport au temps, entre l'électrode de travail (WE) ou la contre-électrode (CE), tandis que la tension entre l'électrode de référence (RE) et l'électrode de travail (WE) peut varier en fonction du temps et s'adapter à cette situation sans toutefois atteindre zéro.

3. Procédé selon l'une quelconque des revendications 1 ou 2, dans lequel le courant circulant entre l'électrode de travail et la contre-électrode est réduit de façon régulée, en particulier pendant l'étape I, tandis que la tension entre l'électrode de travail et l'électrode de référence reste inchangée, dans lequel la régulation, en particulier pendant l'étape I, est de préférence effectuée à l'aide d'une résistance adaptable et réglable (11) entre l'électrode de travail (WE) et la contre-électrode (CE), dans lequel la régulation de cette résistance (11) est de préférence effectuée à l'aide d'une boucle d'asservissement par la mesure du courant dans la trajectoire entre l'électrode de travail (WE) et la contre-électrode (CE).

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel, pendant l'intervalle de temps de dépôt (tA), la tension est régulée de façon à être constante, de préférence dans une gamme de tolérance d'au maximum ± 0,1 V, le plus préférablement dans une gamme de tolérance d'au maximum ± 500 μV.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel, pendant l'intervalle de relaxation (tB), le courant est maintenu constant, de préférence dans une gamme de tolérance équivalente à une densité de courant sur le substrat d'au maximum ± 10 mA/cm^2, le plus préférablement dans une gamme de tolérance d'au maximum ± 1 μA/cm^2.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel, pendant l'intervalle de relaxation (tB), le courant est nul, de préférence dans une gamme de tolérance équivalente à une densité de courant sur le substrat d'au maximum ± 10 mA/cm^2, le plus préférablement dans une gamme de tolérance d'au maximum ± 1 μA/cm^2.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel, pendant l'intervalle de temps de dépôt (tA), la valeur absolue de la tension est supérieure au potentiel de nucléation de la substance réactive, de préférence d'au moins 0,1 V ou dans la gamme de 0,1 à 3,0 V, le plus préférablement dans la gamme de 0,4 à 1,0 V.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'intervalle de temps de dépôt (tA) se situe dans la gamme de 1 μs à 60 μs, de préférence dans la gamme de 1 ms à 1 s, le plus préférablement dans la gamme de 1 à 200 ms.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'intervalle de temps de relaxation (tB) se situe dans la gamme de 1 μs à 60 μs, de préférence dans la gamme de 1 ms à 30 s, le plus préférablement dans la gamme de 1 à 5 s.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le cycle de service de l'intervalle de temps de dépôt (tA) à l'intervalle de temps de relaxation (tB) est inférieur à 80 %, ou inférieur à 50 %, de préférence inférieur à 25 %, le plus préférablement inférieur à 10 %.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel la stoechiométrie de l'alliage déposé et/ou d'un composé chimique est contrôlée à l'aide d'au moins un paramètre adapté correspondant choisi dans le groupe suivant : valeur de tension et/ou longueur (tA, tB) de l'intervalle de temps de dépôt et/ou de relaxation ; cycle de service, densité de courant, rapport de concentration ionique des matières premières de l'alliage/du composé dissous sous forme d'ions dans l'électrolyte (1).

12. Utilisation d'un procédé selon l'une quelconque des revendications précédentes pour déposer un matériau semi-conducteur, un matériau thermoélectrique ou un matériau magnétique, de préférence sur la base d'au moins l'un des matériaux choisis dans le groupe suivant : $Bi_{2+x}Te_{3-x}$, CuInSe, BiSbTe, BiSeTe, SbTe, GeTe, AgSe, PbTe, TeAgGeSb, AgSb, SnTe, CuSe, ZnHgSe, PbCd ou CdTe, CiNiFe ou CoFe sur un substrat.

13. Utilisation selon la revendication 12 pour déposer $Bi_{2+x}Te_{3-x}$, dans laquelle la tension pendant l'intervalle de temps de dépôt (tA) est choisie dans la gamme de -10,0 à -0,1 V, de préférence de -1,0 à -0,3 V, et dans laquelle, pendant l'intervalle de temps de relaxation, circule un courant régulé de I = 0, dans laquelle, de préférence, pour déposer $Bi_{2+x}Te_{3-x}$ de type p, le rapport de $[HTeO_{2+}]$ à $[Bi_{3+}]$ dans l'électrolyte (1) est choisi de telle sorte que le rapport atomique Te:Be dans le dépôt est inférieur à 1,6, ou inférieur à 1,5, ou inférieur à 1,25, et dans laquelle, encore plus préférablement, la solution électrolytique comprend au moins 1,5 M de HNO_3, au moins 30 mM de $[HTeO_{2+}]$ et/ou au moins 30 mM de $[Bi_{3+}]$.

14. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel, avant de commencer l'une quelconque des étapes I et/ou II, l'électrolyte liquide (1) est préparé en fournissant une solution de HNO_3 concentrée, de préférence dans une concentration supérieure à 70 %, en chauffant jusqu'à la température d'ébullition ou jusqu'à une température pas supérieure à 40 °C au-dessous du point d'ébullition, de préférence pas supérieure à 5 °C au-dessous du point d'ébullition, en ajoutant du TeO_2 en quantité souhaitée, en agitant la solution correspondante et en ajoutant de l'eau à la solution jusqu'à dissolution quasi-complète du TeO_2, puis en diminuant facultativement la température au-dessous de 80 °C, en ajoutant du Bi_2O_3 en quantité souhaitée, en agitant jusqu'à dissolution de tous les constituants, en ajoutant de l'eau jusqu'à obtenir une concentration souhaitée en HNO_3, de préférence de l'ordre de 2 M.

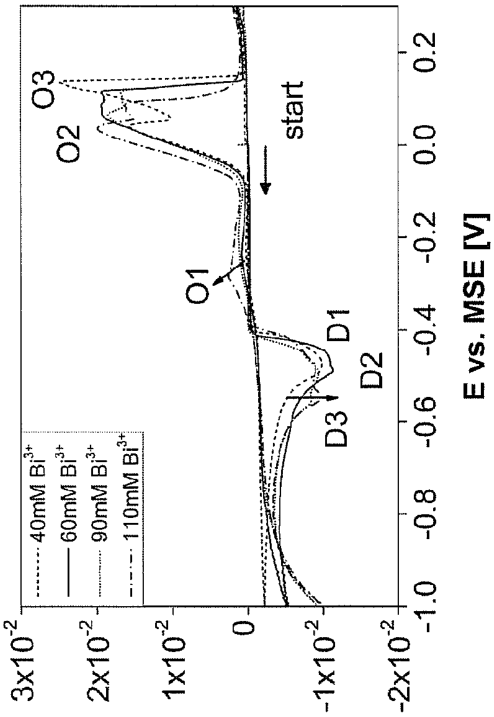
I [A]
3x10^-2
2x10^-2
1x10^-2
0
-1x10^-2
-2x10^-2
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
E vs. MSE [V]
40mM Bi3+
60mM Bi3+
90mM Bi3+
110mM Bi3+
O1
O2
O3
D1
D2
D3
start

Fig. 1

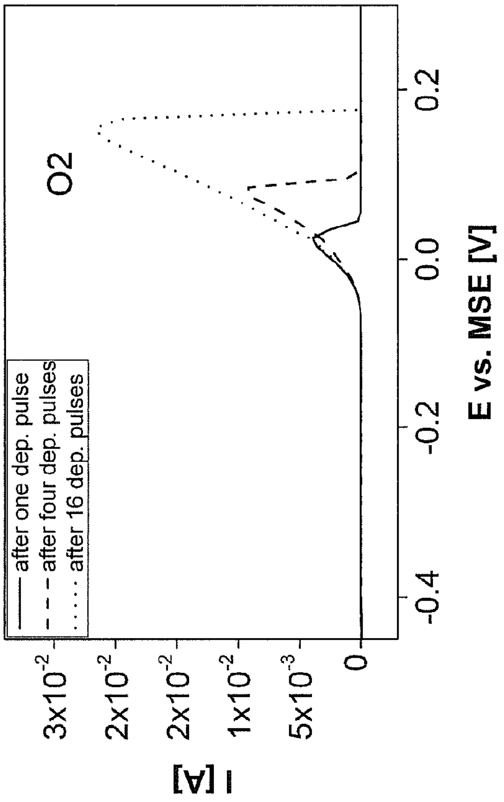
I [A]
3x10^-2
2x10^-2
2x10^-2
1x10^-2
5x10^-3
0
-0.4
-0.2
0.0
0.2
E vs. MSE [V]
after one dep. pulse
after four dep. pulses
after 16 dep. pulses
O2

Fig. 4

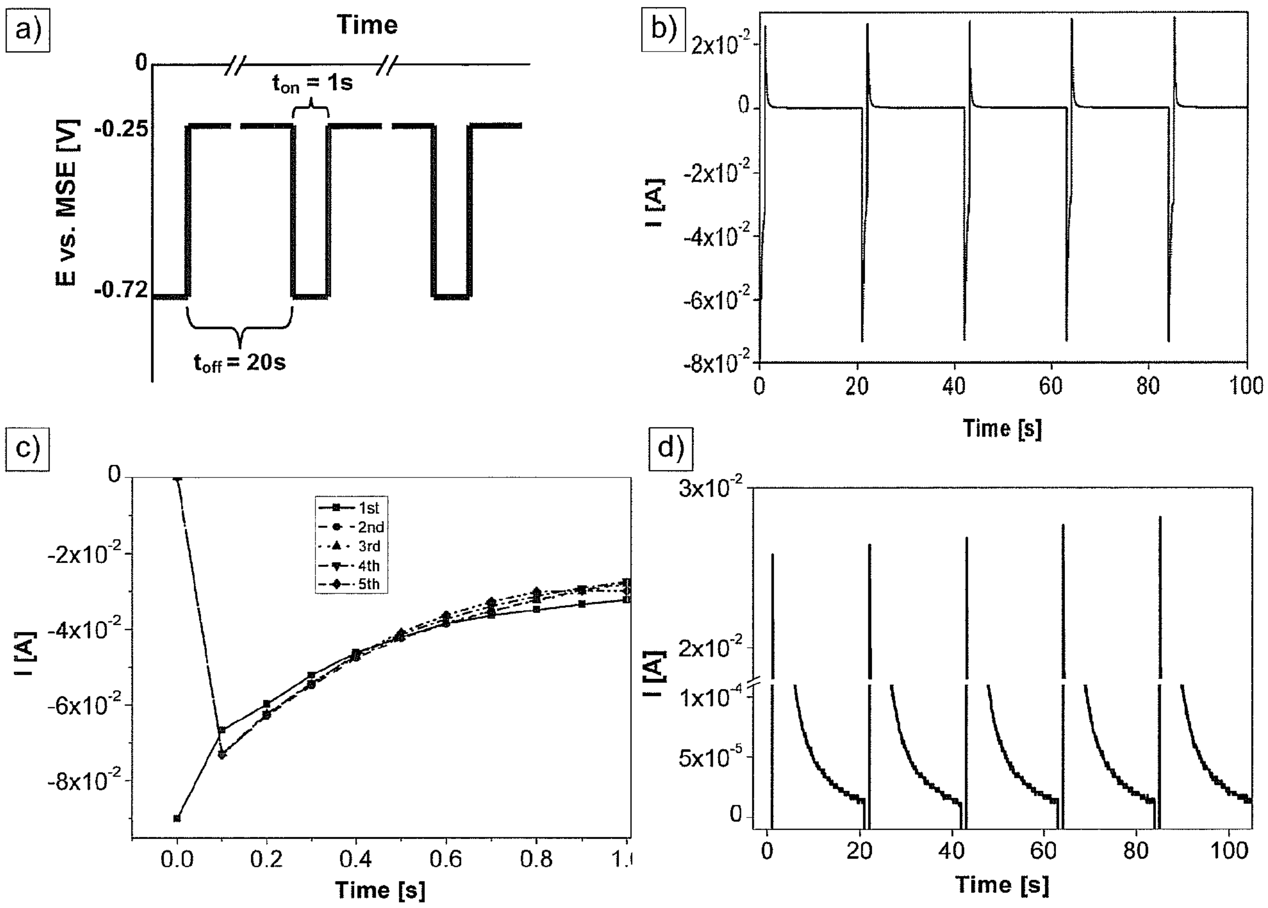
a)
Time
0
-0.25
-0.72
E vs. MSE [V]
t_{on} = 1s
t_{off} = 20s
b)
I [A]
2x10^{-2}
0
-2x10^{-2}
-4x10^{-2}
-6x10^{-2}
-8x10^{-2}
0
20
40
60
80
100
Time [s]
c)
I [A]
0
-2x10^{-2}
-4x10^{-2}
-6x10^{-2}
-8x10^{-2}
1st
2nd
3rd
4th
5th
0.0
0.2
0.4
0.6
0.8
1.0
Time [s]
d)
I [A]
3x10^{-2}
2x10^{-2}
1x10^{-4}
5x10^{-5}
0
0
20
40
60
80
100
Time [s]

Fig. 2

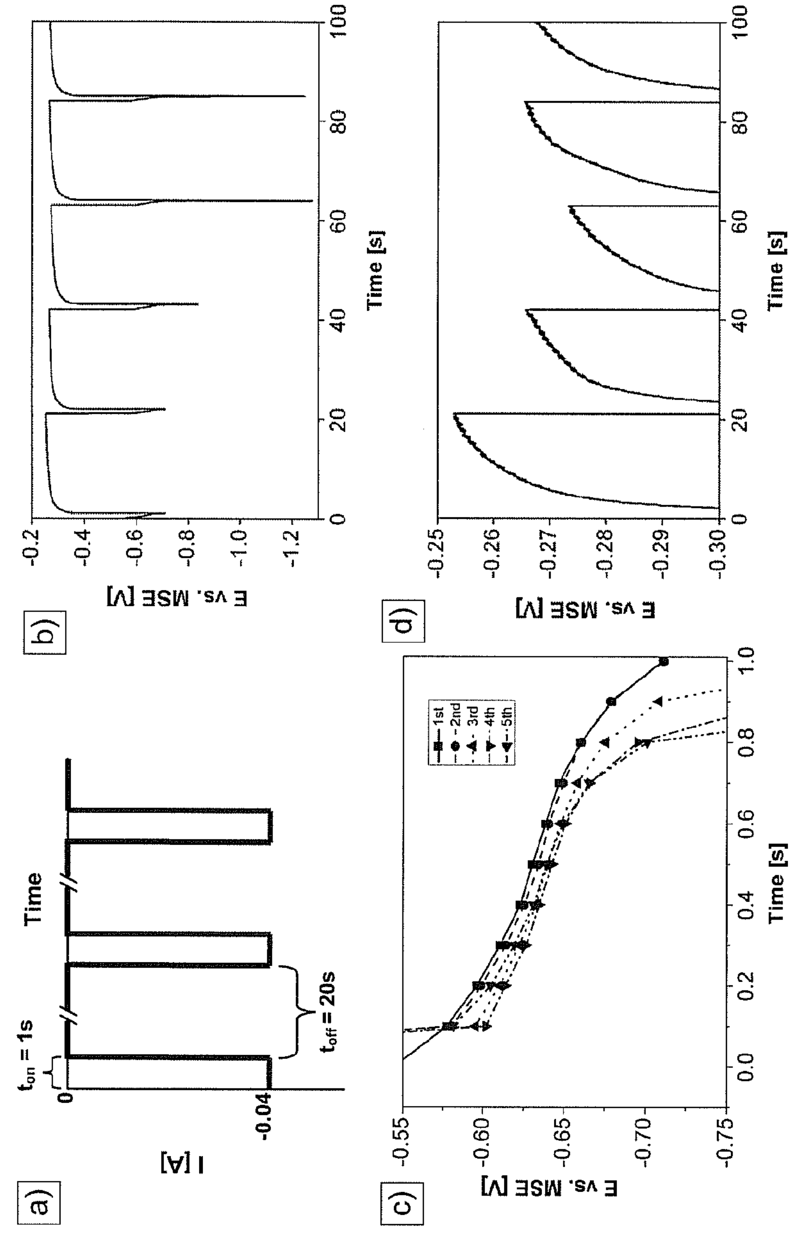
a)
I [A]
0
-0.04
t_on = 1s
t_off = 20s
Time
b)
E vs. MSE [V]
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
0
20
40
60
80
100
Time [s]
c)
E vs. MSE [V]
-0.55
-0.60
-0.65
-0.70
-0.75
0.0
0.2
0.4
0.6
0.8
1.0
Time [s]
1st
2nd
3rd
4th
5th
d)
E vs. MSE [V]
-0.25
-0.26
-0.27
-0.28
-0.29
-0.30
0
20
40
60
80
100
Time [s]

Fig. 3

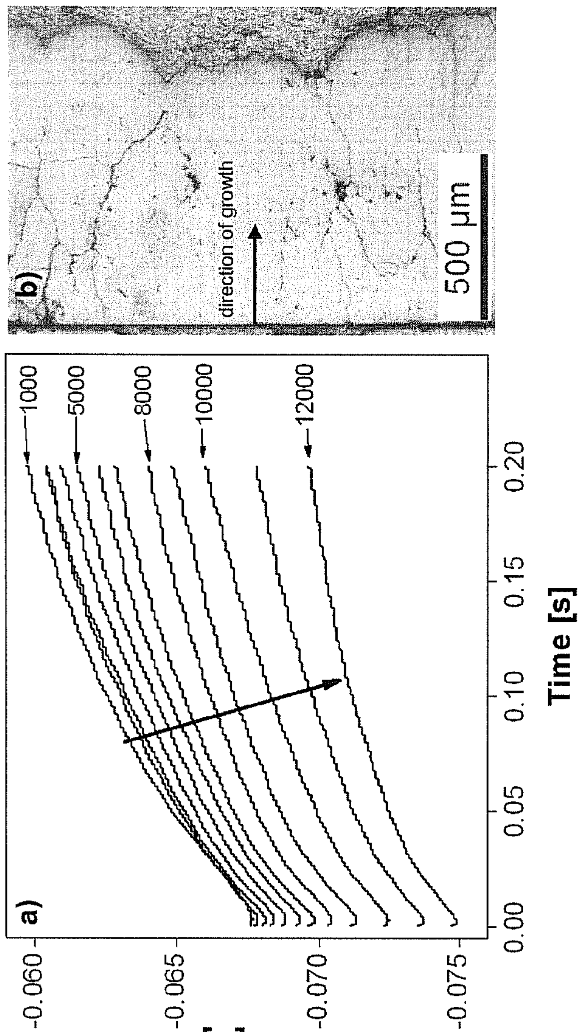
a)
I [A]
-0.060
-0.065
-0.070
-0.075
0.00
0.05
0.10
0.15
0.20
Time [s]
1000
5000
8000
10000
12000
b)
direction of growth
500 µm

Fig. 5

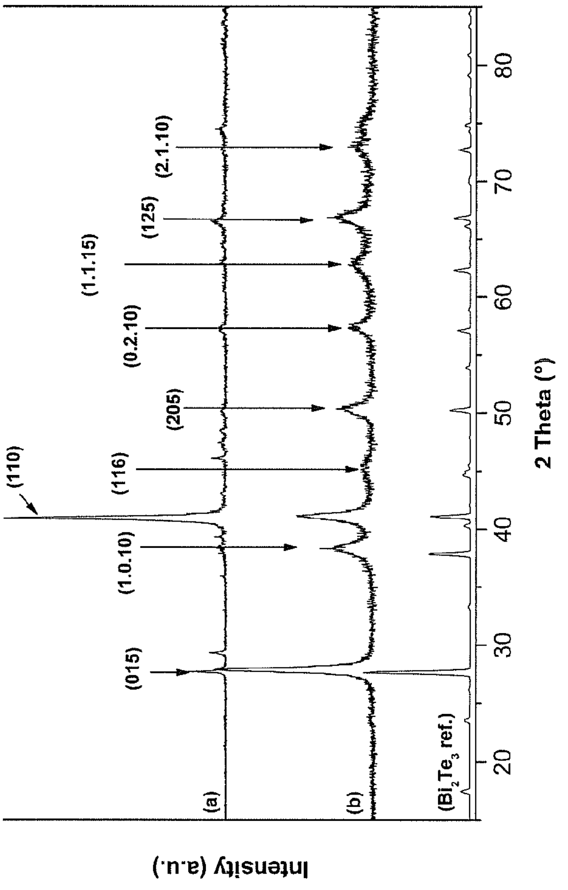
Intensity (a.u.)
2 Theta (°)
20
30
40
50
60
70
80
(a)
(b)
(Bi_2Te_3 ref.)
(015)
(1.0.10)
(110)
(116)
(205)
(0.2.10)
(1.1.15)
(125)
(2.1.10)

Fig. 6

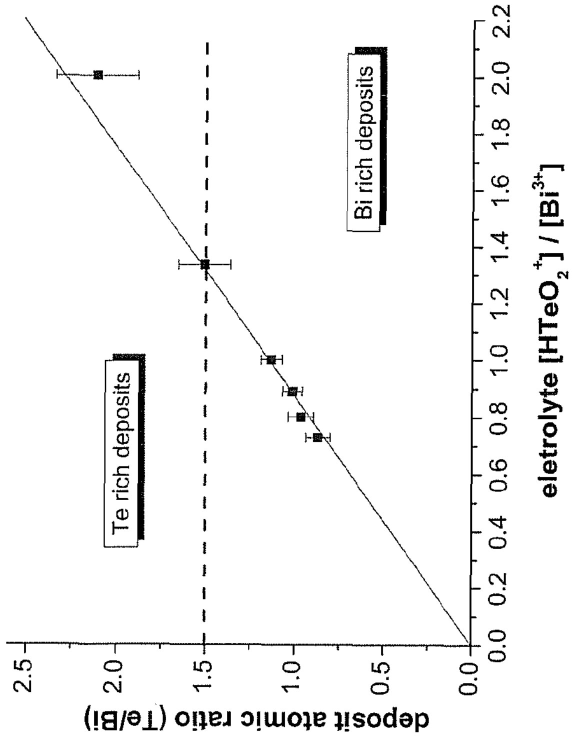
deposit atomic ratio (Te/Bi)
0.0
0.5
1.0
1.5
2.0
2.5
eletrolyte [HTeO$_2^+$] / [Bi^{3+}]
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Te rich deposits
Bi rich deposits

Fig. 7

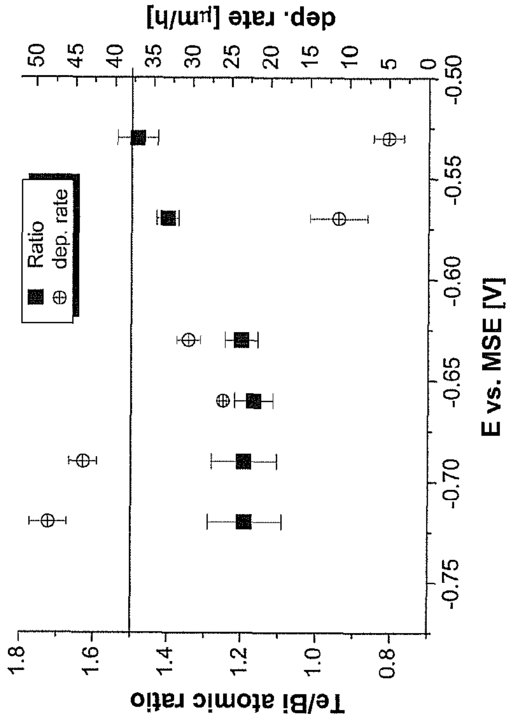
Te/Bi atomic ratio
0.8
1.0
1.2
1.4
1.6
1.8
dep. rate [μm/h]
0
5
10
15
20
25
30
35
40
45
50
E vs. MSE [V]
-0.50
-0.55
-0.60
-0.65
-0.70
-0.75
■ Ratio
⊕ dep. rate

Fig. 9

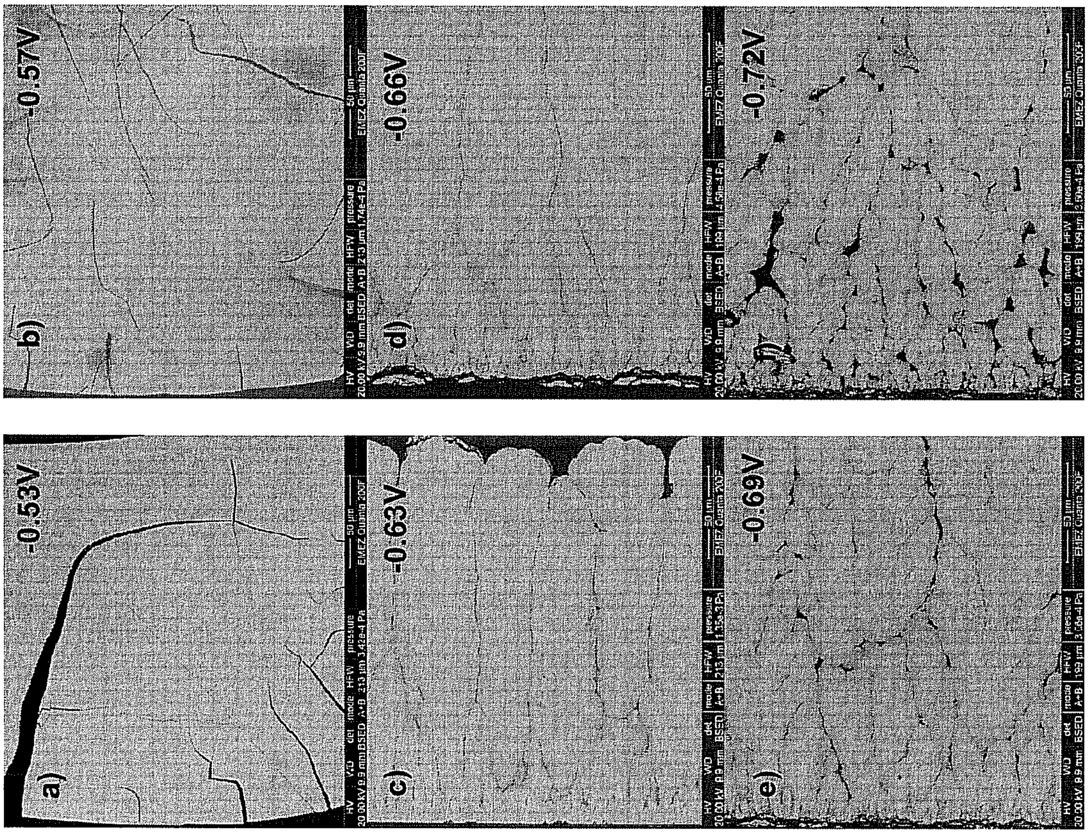

Fig. 8

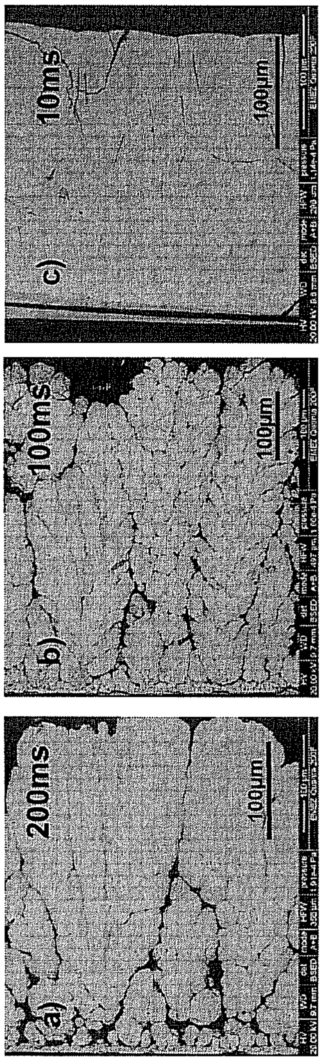
a)
200ms
100µm
b)
100ms
100µm
c)
10ms
100µm

Fig. 10

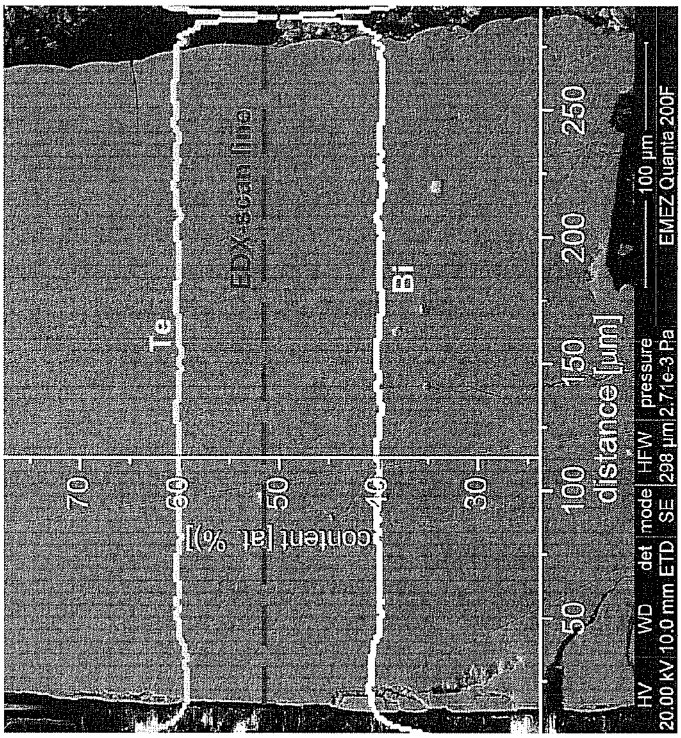
Te
Bi
EDX-scan line
content [at %]
70
60
50
40
30
50
100
150
200
250
distance [µm]
HV 20.00 kV
WD 10.0 mm
det ETD
mode SE
HFW 298 µm
pressure 2.71e-3 Pa
100 µm
EMEZ Quanta 200F

Fig. 11

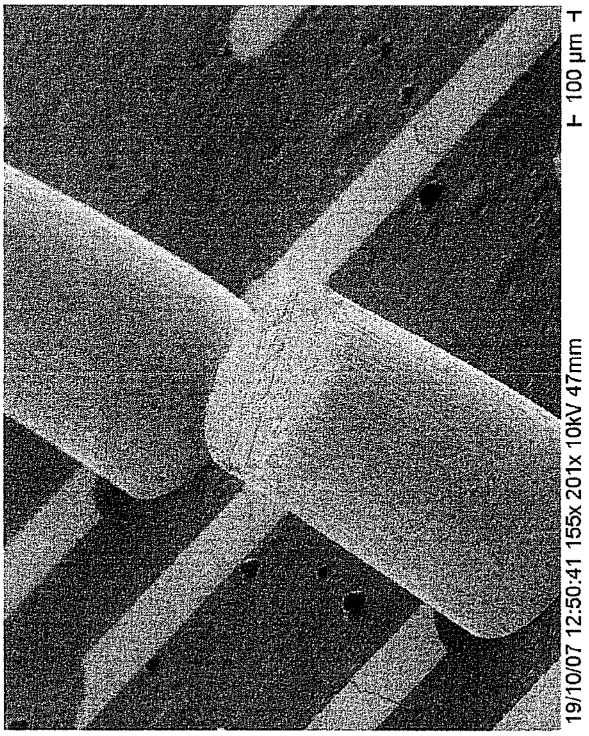
19/10/07 12:50:41 155x 201x 10kV 47mm
100 µm

Fig. 12

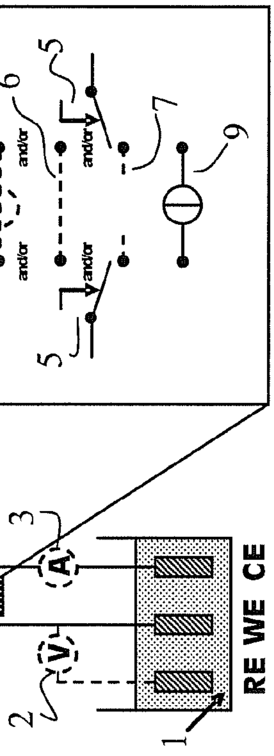
1
2
3
4
4
5
5
6
7
8
9
V
A
RE WE CE
and/or
and/or
and/or
and/or

Fig. 13

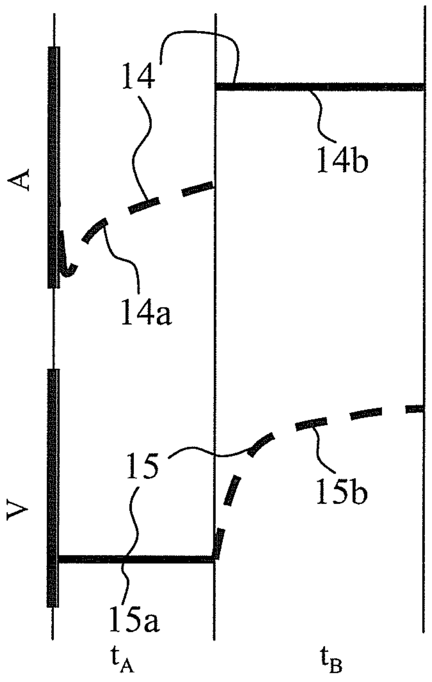

Fig. 14

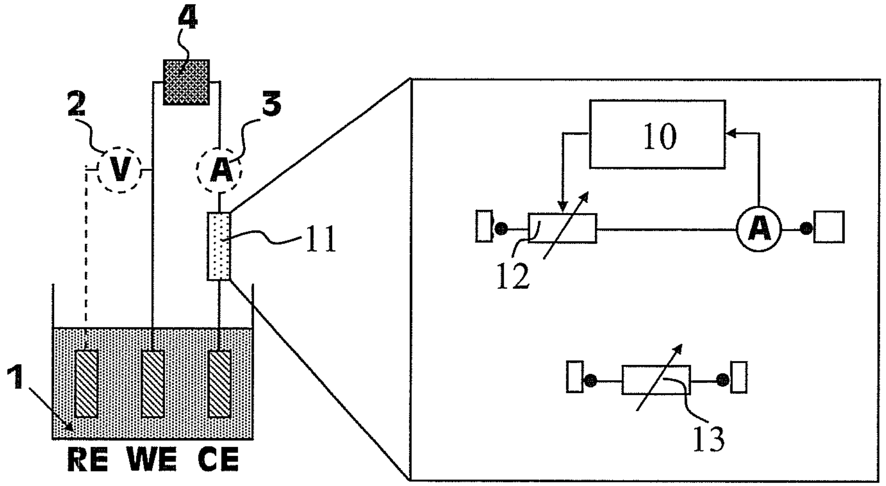

Fig. 15

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 6881318 B **[0030]**

Non-patent literature cited in the description

- **CH. BONHOTE et al.** Microstructure of Ni-Cu multilayers electrodeposited from a citrate electrolyte. *Electrochimica Acta,* vol. 42 (15), 2407-2417 **[0016]**
- **LI et al.** Study of electrodeposition of bismuth telluride by voltametric methods and in-situ electrochemical quartz crystal microbalance method. *Thin Solid Films,* 2007, vol. 515, 7847-7854 **[0016]**