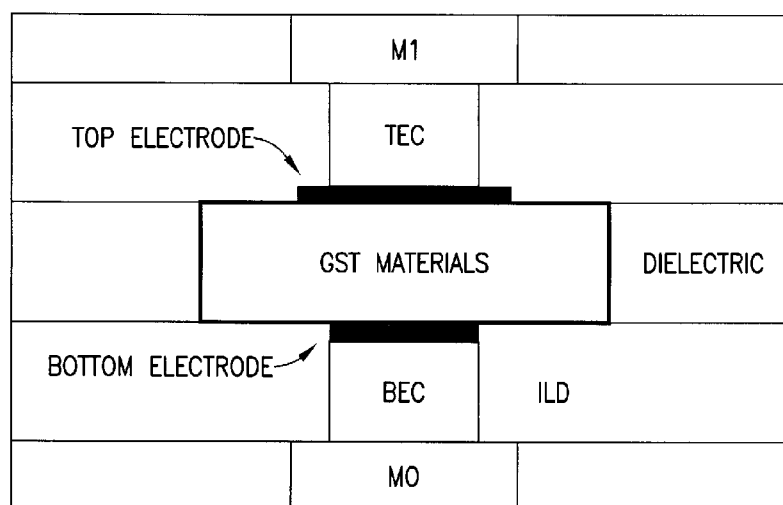




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(54) **Title:** OXIC GERMANIUM-ANTIMONY-TELLURIUM MATERIAL AND PHASE CHANGE MEMORY COMPRISING SAME

**FIG.1**

(57) **Abstract:** A GST material selected from among: (a) GST materials having oxygen incorporated therein at concentration of from 0.10 to 10 atomic %, based on atomic weight of the GST material; and (b) GST materials having a reset current of less than 0.1 milliamps when the GST material is comprised in a GST phase change random access memory device. The GST material can be formed by vapor deposition processes, and utilized in phase change memory devices of varied types to provide devices having reset current values of 0.1 milliamps and lower.



OXIC GERMANIUM-ANTIMONY-TELLURIUM MATERIAL AND PHASE CHANGE MEMORY COMPRISING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The benefit of priority under 35 USC 119 of U.S. Provisional Patent Application 61/471,188 filed April 3, 2011 in the name of Jun-Fei Zheng for “OXIC GERMANIUM-ANTIMONY-TELLURIUM MATERIAL AND PHASE CHANGE MEMORY COMPRISING SAME,” the benefit of priority under 35 USC 119 of U.S. Provisional Patent Application 61/511,282 filed July 25, 2011 in the name of Jun-Fei Zheng for “OXIC GERMANIUM-ANTIMONY-TELLURIUM MATERIAL AND PHASE CHANGE MEMORY COMPRISING SAME,” the benefit of priority under 35 USC 119 of U.S. Provisional Patent Application 61/524,953 filed August 18, 2011 in the name of Jun-Fei Zheng for “OXIC GERMANIUM-ANTIMONY-TELLURIUM MATERIAL AND PHASE CHANGE MEMORY COMPRISING SAME,” the benefit of priority under 35 USC 119 of U.S. Provisional Patent Application 61/527,122 filed August 25, 2011 in the name of Jun-Fei Zheng for “OXIC GERMANIUM-ANTIMONY-TELLURIUM MATERIAL AND PHASE CHANGE MEMORY COMPRISING SAME,” the benefit of priority under 35 USC 119 of U.S. Provisional Patent Application 61/527,602 filed August 25, 2011 in the name of Jun-Fei Zheng for “OXIC GERMANIUM-ANTIMONY-TELLURIUM MATERIAL AND PHASE CHANGE MEMORY COMPRISING SAME,” and the benefit of priority under 35 USC 119 of U.S. Provisional Patent Application 61/528,138 filed August 26, 2011 in the name of Jun-Fei Zheng for “OXIC GERMANIUM-ANTIMONY-TELLURIUM MATERIAL AND PHASE CHANGE MEMORY COMPRISING SAME,” is hereby claimed. The disclosures of such related U.S. provisional applications are hereby incorporated herein by reference in their respective entireties, for all purposes.

FIELD

[0002] The present disclosure relates to oxide germanium-antimony-tellurium (GeSbTe, or GST) material useful in manufacturing phase change memory devices, and to germanium antimony telluride phase change memory devices that are manufactured using such material.

DESCRIPTION OF THE RELATED ART

[0003] Phase change memory (PCM) is a type of non-volatile computer memory that utilizes differences in the electrical resistivity of the crystalline and amorphous phase states of memory

materials. Devices that incorporate PCM typically comprise substrates on which a particular memory material (e.g., a chalcogenide) is deposited. The memory material is typically deposited within structures (such as holes, trenches, or the like) in or on the surfaces of the substrate. Patterned electrodes are also deposited on the substrate to allow for the conduction of current. Current is conducted through the deposited memory material, with the level of current being dependent on the resistivity and heating efficiency of the memory material and its alloy properties incident to phase change.

[0001] One memory material used in the manufacture of PCM devices is germanium antimony telluride (GST). GST materials can in principle function very effectively as phase change material for a volume, v , having characteristic dimensions as small as 5 nm. The trend is to make PCM devices based on GST with characteristic dimensions in the regime of 30 to 10 nm or less in future generation devices.

[0002] The deposition of GST materials to form films for PCM applications can be carried out using vapor deposition processes, such as chemical vapor deposition (CVD), metalorganic chemical vapor deposition (MOCVD), atomic layer deposition (ALD), and other vapor phase techniques.

[0003] PCM technology has the potential to expand commercially into dynamic random access memory (DRAM) and storage class memory (SCM) applications. These applications require long cycling endurance and fast write speeds while maintaining sufficient data retention character, as well as maintaining a low reset current at small device scales and high aspect ratios. In this respect, alloy compositions and device structure have a substantially interrelated impact on the PCM performance of the product device. The ability to conformally deposit GST films enables improved PCM cell heating efficiency with lower reset current, by minimizing the amount of GST film material in the cell and reducing heat loss.

[0004] Significant efforts are being made to improve performance of PCM alloy compositions and device performance (e.g., low reset current, device speed, cycle endurance), relative to that achieved by the GST225 alloy (atomic composition 22.5% Ge, 22.5% Sb, and 55% Te) currently used as a benchmark standard for PCM films and devices. Reset current is a particularly critical parameter and is a major focus of these ongoing efforts.

[0005] There is accordingly a compelling need for improved GST films and phase change microelectronic devices utilizing same in PCRAM applications, to enable operation of such devices at significantly reduced reset current values, in relation to the high reset current values, e.g., > 1 mA, that characterize many currently available GST PCRAM devices.

SUMMARY

[0006] The present disclosure relates to GST material useful in manufacturing phase change memory devices, and to germanium antimony telluride phase change memory devices that are manufactured using such material.

[0007] In one aspect, the disclosure relates to a GST material selected from among:

(a) GST materials having oxygen incorporated therein at concentration of from 0.10 to 10 atomic % of the GST material; and

(b) GST materials having a reset current of less than 0.1 milliamps when the GST material is comprised in a GST phase change random access memory device.

[0008] In another aspect, the disclosure relates to a GST material containing 1-3 atomic % oxygen, and having reset current below 0.1 mA in a PCRAM device.

[0009] In a further aspect, the disclosure relates to a method of making a phase change material, comprising forming a germanium-antimony-tellurium (GST) material, and incorporating oxygen therein at concentration of from 0.10 to 10 atomic % of the GST material.

[0010] A further aspect of the disclosure relates to a method of making a phase change material, comprising forming a germanium-antimony-tellurium (GST) material, and incorporating oxygen therein at sufficient concentration to yield a reset current of less than 0.1 milliamps when the GST material is comprised in a GST phase change random access memory device.

[0011] A still further aspect of the disclosure relates to a phase change memory device, comprising: a substrate; a hole structure extending from a first surface of the substrate to a second surface of the substrate; GST material of the present disclosure, deposited in the hole structure; and first and second electrodes located at opposing ends of the hole structure.

[0012] Yet another aspect the disclosure relates to a GST alloy having a reset speed of less than 50 ns and a reset current of less than 1.2 mA.

[0013] The disclosure in another aspect relates to a GST phase change memory device, comprising a hole structure having a size dimension below 15 nm, with an oxygen-containing GST material therein having a set time of less than 15 ns.

[0014] In a further aspect, the disclosure relates to a GST phase change memory device, comprising a hole structure having a size dimension below 15 nm with an oxygen-containing GST material therein having a set speed of less than 100 ns.

[0015] Yet another aspect of the disclosure relates to an oxygen-containing GST material having a set time of less than 15 ns.

[0016] A further aspect the disclosure relates to an oxygen-containing GST material having a set speed of less than 100 ns.

[0017] In another aspect, the disclosure relates to a GST material having a set time of less than 15 ns, a set speed of less than 100 ns, and a resistivity of less than 0.01 Ω -cm.

[0018] A further aspect of the disclosure relates to a GST material having a programming cycle endurance greater than 5×10^8 , a set time of 20ns or less, and <20ns set speed.

[0019] Another aspect of the disclosure relates to a GST PCM device comprising a GST material according to claim 63.

[0020] Another aspect of the disclosure relates to a method of making a GST film having resistivity below 0.01 Ω -cm, said method comprising incorporating oxygen in said GST film during or after vapor deposition formation thereof, and annealing said GST film having oxygen incorporated therein, at temperature in a range of from 300°C to 375°C for a period of from 2 to 24 hours.

[0021] A still further aspect the disclosure relates to a GST material having at least one of the characteristics of: a set time of less than 15 ns; a set speed of less than 100 ns; and a resistivity of less than 0.01 Ω -cm, wherein said GST material has been formed by a process comprising: vaporizing germanium, antimony and tellurium precursors for the germanium antimony telluride material, to form corresponding precursor vapor, with such precursors comprising $\text{Ge}[\text{Pr}^i\text{NC}(\text{n-Bu})\text{NPr}^i]_2$ as the germanium precursor, tris(dimethylamido)antimony as the antimony precursor, and $\text{Te}(\text{tBu})_2$ as the tellurium precursor; heating the tellurium precursor vapor to temperature in a range of from 180°C to 450°C for activation thereof, separate from the other precursors; contacting germanium precursor vapor, antimony precursor vapor, and activated tellurium precursor vapor with a substrate under conditions enabling formation of the germanium antimony telluride material on the substrate, wherein the substrate during such contacting is at temperature in a range of from 110°C to 300°C.

[0022] Yet another aspect of the disclosure relates to a GST material having a 36-14-50 GST alloy composition.

[0023] Other aspects, features and embodiments of the disclosure will be more fully apparent from the ensuing description and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] FIG. 1 is a schematic representation of a PCM GST device structure according to one embodiment of the present disclosure.

[0025] FIG. 2 is a schematic of a GST device structure according to another embodiment of the present disclosure, showing the GST plug, top electrode, bottom electrode, interlayer dielectric and associated layers of the device.

[0026] FIG. 3 is a graph showing oxygen and carbon concentration, in atomic percent, as a function of depth, in nanometers (nm) of an oxidic GST film according to one embodiment of the

present disclosure, and germanium, antimony, tellurium and silicon concentrations, in arbitrary intensity units, as a function of depth of the GST film, in nanometers (nm).

[0027] FIG. 4 is a graph showing oxygen and carbon concentration, in atomic percent, as a function of depth, in nanometers (nm) of an oxide GST film according to another embodiment of the present disclosure, and germanium, antimony, tellurium and silicon concentrations, in atomic percent, as a function of depth of the GST film, in nanometers (nm).

[0028] FIG. 5 is a graph of resistance, in ohms, as a function of reset current, in milliamperes (mA), for an oxide GST film-based PCM device of the present disclosure, showing a dynamic range for the device of $\sim 100 \times$, and a reset current of $< 0.2 \text{ mA}$.

[0029] FIG. 6 is a graph of reset current, in milliamperes (mA), as a function of voltage, in volts, for an oxide GST material of the present disclosure, wherein $V_t = 1.03 \text{ volts}$, $V_h = 0.57 \text{ volt}$, and $dV/dI = 3.31 \text{ k}\Omega$.

[0030] FIG. 7 is a graph of resistance, in ohms, as a function of reset current, in milliamperes (mA), for an oxide GST film-based PCM device of the present disclosure, showing curves for 0, 1, 2, 5, 10, 20, 50, 100, 200, 500 and 1000 cycles of phase change.

[0031] FIG. 8 is a graph of reset current, in milliamperes (mA), as a function of voltage, in volts, for an oxide GST material of the present disclosure, wherein $V_t = 0.98 \text{ volts}$, $V_h = 0.59 \text{ volt}$, and $dV/dI = 7.06 \text{ k}\Omega$.

[0032] FIG. 9 is a graph of the parameters V_t (Δ), V_h ($\circ$), dV/dI , in $\text{k}\Omega$ ($\times$), $\text{Log } R$ ($\diamond$), $\text{Log } R$ in Ohms ($\square$), as a function of the number of phase change cycles, for an oxide GST material of the present disclosure.

[0033] FIG. 10 is a graph of resistance in ohms (Ω) for R_{set} ($\square$) and R_{reset} ($\diamond$), as a function of fall time, in nanoseconds, (ns), showing a $\frac{1}{2}$ full fall time set speed on the order of 250 nanoseconds, depending on the demarcation level.

[0034] FIG. 11 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$), R_{set} ($\bullet$) and $R_{\text{demarcation}}$ ($\square$).

[0035] FIG. 12 is a graph of cumulative probability (%) as a function of device set time, in nanoseconds (ns), for such GST alloy test device, with a vertical dashed line representation of the 50 ns set time.

[0036] FIG. 13 is a graph of V (volts), dV/dI (Kohms) and $I_{\text{rs,sat}}$ (mA), and read resistance (ohms), as a function of number of cycles, showing the results of a cycle endurance test for $\text{Ge}_{0.24}\text{Sb}_{0.19}\text{Te}_{0.58}$ alloy material.

[0037] FIG. 14 is a graph of V (volts), dV/dI (Kohms) and $I_{\text{rs,sat}}$ (mA), and read resistance (ohms), as a function of number of cycles, showing the results of a corresponding cycle endurance test for the same $\text{Ge}_{0.24}\text{Sb}_{0.19}\text{Te}_{0.58}$ alloy material that was used to generate the data of FIG. 13, wherein the data are direct pulse results that were generated without using a quench circuit.

[0038] FIG. 15(a) is a cross-sectional scanning electron micrograph (SEM) image of an MOCVD GST alloy filling a hole of 15 nm size, and FIG. 15(b) is a cross-sectional scanning electron micrograph (SEM) image of an MOCVD GST alloy filling a hole of ~20 nm size.

[0039] FIG. 16(a) is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$), R_{set} ($\bullet$) and $R_{\text{demarcation}}$ (—), in a 135 nm device. FIG. 16(b) is a speed test curve showing a phase change memory made with MOCVD GST taking only ~12 ns to reach ~20k Ω set resistance level from reset resistance level of ~1M Ω . FIG. 16(c) shows cycle endurance of such MOCVD GST material as measured at 50 ns set time.

[0040] FIG. 17 is a graph of resistivity, in $\Omega\text{-cm}$, as a function of annealing temperature, in degrees Centigrade, for illustrative oxygen-containing porous GST films whose micrographs are shown in FIGS. 18-21.

[0041] FIG. 18 is a micrograph of a porous GST film, which as grown had a resistivity value greater than 32 $\Omega\text{-cm}$. Such film had a 350 Å thickness.

[0042] FIG. 19 is a SEM micrograph of a corresponding oxygen-containing porous GST film after annealing at 300°C, as a result of which the film had a resistivity of $0.018 \pm 0.0014 \Omega\text{-cm}$.

[0043] FIG. 20 is a SEM micrograph of a corresponding oxygen-containing porous GST film after annealing at 350°C, in consequence of which the film had a resistivity of $0.00352 \pm 0.00006 \Omega\text{-cm}$.

[0044] FIG. 21 is a SEM micrograph of a corresponding oxygen-containing porous GST film after annealing at 375°C, which resulted in the film having a resistivity of $0.00238 \pm 0.00036 \Omega\text{-cm}$, albeit with a less desirable morphology, as compared with films annealed at lower temperatures.

[0045] FIG. 22 is a graph of oxygen and carbon concentration, in atomic percent, and germanium, tellurium, antimony, and silicon intensity, in arbitrary units, as a function of material depth in the GST material, for an MOCVD GST 225 alloy containing ~ 1-2% oxygen.

[0046] FIG. 23 is a graph of oxygen and carbon concentration, in atomic percent, and germanium, tellurium, antimony, and silicon intensity, in arbitrary units, as a function of material depth in the GST material, for an MOCVD GST 325 alloy containing ~ 1-2% oxygen.

[0047] FIG. 24 is a graph of resistivity, in $\Omega\text{-cm}$, as a function of annealing temperature, in degrees Centigrade, for oxide GST 225, GST 325, and GST 415 alloys, showing that the low resistivities were obtained in such oxide alloys by annealing at temperature in a range of from 300 to 400°C.

[0048] FIG. 25 is a graph of oxygen and carbon concentration, in atomic percent, and germanium, tellurium, antimony, and silicon intensity, in arbitrary units, as a function of material depth in the GST material, for an MOCVD GST 415 alloy containing ~ 1- 10% oxygen.

[0049] FIG. 26 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$) and R_{set} ($\bullet$) in a 112 nm device after annealing of a GST material having an 86 ns set speed, at 375°C for 24 hours in argon gas.

[0050] FIG. 27 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$), R_{set} ($\bullet$) and $R_{\text{demarcation}}$ (—) (ohms), in a 135 nm device after annealing of an oxyc GST material having a 55 ns set speed, at 375°C for 24 hours in argon gas.

[0051] FIG. 28 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$) and R_{set} ($\bullet$) in a 112 nm device after annealing of a 325 GST material having a 215 ns set speed, at 375°C for 24 hours in argon gas.

[0052] FIG. 29 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$), R_{set} ($\bullet$) and $R_{\text{demarcation}}$ (—) (ohms), in a 135 nm device after annealing of an oxyc 325 GST material having a 111 ns set speed, at 375°C for 24 hours in argon gas.

[0053] FIG. 30 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$) and R_{set} ($\bullet$) in an ~100 nm device including a 415 GST material having an ~80 ns set speed.

[0054] FIG. 31 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$), R_{set} ($\bullet$) and $R_{\text{demarcation}}$ (—) (ohms), in an ~ 100 nm device after annealing of a 415 GST material at 375°C for 24 hours in argon gas.

DETAILED DESCRIPTION

[0055] As used herein, the term “film” refers to a layer of deposited material having a thickness below 1000 micrometers, e.g., from such value down to atomic monolayer thickness values. In various embodiments, film thicknesses of deposited material layers in the practice of the invention may for example be below 100, 10, or 1 micrometers, or in various thin film regimes below 200, 100, or 50 nanometers, depending on the specific application involved. As used herein, the term “thin film” means a layer of a material having a thickness below 1 micrometer.

[0056] As used herein and in the appended claims, the singular forms “a”, “and”, and “the” include plural referents unless the context clearly dictates otherwise.

[0057] Unless otherwise specified, all film compositions herein are specified in terms of atomic percentages of the film components, wherein the sum of all atomic percentages of all components in the film totals to 100 atomic %.

[0058] It will be appreciated that the method and GST structures of the present disclosure can be effectuated in hole, trench, cavity or other structures of widely varying dimensions, and that the ensuing description is directed to illustrative examples and disclosure.

[0059] It will also be appreciated that the method and GST structures of the present disclosure can be effectuated utilizing flat GST films that are in contact with bottom electrodes of fixed size with respect to their contact area, to provide phase change memory cell arrangements that do not require confined structures.

[0060] The present disclosure is based on the discovery that reset current of a germanium-antimony-tellurium (GST) phase change memory (PCM) device, e.g., a phase change random access memory (PCRAM) device, can be reduced by 90% or more, in relation to current reset values of presently available GST PCRAM devices, by incorporation of oxygen in the GST material, e.g., at atomic percent levels of from 0.10 to 10% of the GST material comprising same.

[0061] The oxygen can be incorporated in the GST material during formation of the GST material, e.g., by vapor deposition of GST material on a substrate using germanium, antimony and tellurium precursors, in which the GST material formation is carried out with oxygen, ozone, singlet oxygen or other oxygen source in the vapor phase so that oxygen is incorporated in the GST material in the desired amount. Alternatively, the oxygen can be incorporated in the GST material following its formation, e.g., in a pulsed CVD or an ALD process in which oxygen or oxygen-containing gas is contacted with the GST material for such incorporation. In a still further alternative, the oxygen can be incorporated by diffusion of oxygen into films of porous or permeable character. Such diffused oxygen can be in bound form or alternatively in a free form in the film.

[0062] Thus, the oxygen incorporation can be effected by any suitable mechanism, such as oxygen coordination to metal(s) in the GST material, intercalation of oxygen in the GST material, diffusional incorporation in the GST material, etc., and using any suitable methods, such as doping, use of oxidic ambients, co-flow of oxygen or oxygen-containing material during vapor deposition of GST, etc., it being necessary only that the oxidic character of the GST material be such as to reduce the reset current of the material in relation to GST material lacking such oxidic character.

[0063] The oxygenation of the GST material advantageously can be such as to reduce the reset current value by at least 10% in relation to a corresponding non-oxygenated GST material, and more preferably, in other embodiments, can be at least 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90% or 95%, respectively, with any of such percentages differing in magnitude constituting respective end-points of ranges of reset current reduction in other embodiments of the invention, e.g., a reduction of reset current value, in relation to a corresponding non-oxygenated GST material, of from 15% to 90%, from 50% to 95%, from 20% to 65%, etc.

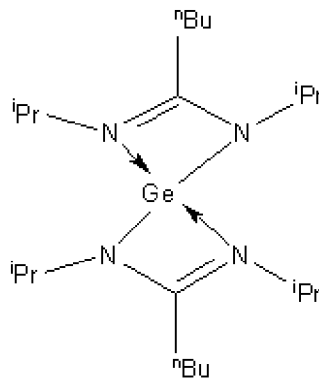
[0064] In other embodiments of the disclosure, the oxygenation of the GST material is such as to reduce the reset current value to a value not exceeding 0.2 mA, and more preferably, in other embodiments, to a value not exceeding 0.19 mA, 0.18 mA, 0.17 mA, 0.16 mA, 0.15 mA, 0.14 mA,

0.13 mA, 0.12 mA, 0.11 mA, 0.10 mA, 0.05 mA, or 0.01 mA, respectively, with any of such values differing in magnitude constituting respective end-points of ranges of reset current values in other embodiments of the invention, e.g., a reset current value of from 0.01 to 0.09 mA, from 0.01 to 0.07 mA, from 0.01 to 0.05 mA, from 0.05 to 0.09 mA, etc.

[0065] The oxygenated GST materials of the disclosure, including the embodiments variously described above, are referred to herein as “oxic GST” materials.

[0066] The PCM structures of the present disclosure can be formed with deposition of the GST material by vapor deposition processes of suitable character that employ appropriate precursors for the respective Ge, Sb and Te components of the GST material.

[0067] In one embodiment of the disclosure, oxygen is incorporated in a GST material by MOCVD with an oxygen-containing ambient during the MOCVD process, using the following germanium, antimony and tellurium precursors:



$\{n\text{BuC}(\text{iPrN})_2\}_2\text{Ge}$,
also referred to as GeM

SbTDMA

tris(dimethylamido)antimony

$\text{Te}(\text{tBu})_2$

di-t-butyl telluride

to produce GST material containing 1-10 atomic % oxygen, as measured by secondary ion mass spectrometry (SIMS) determination, having reset current below 0.1 mA.

[0068] The disclosure in another aspect relates to a phase change memory device, comprising:

a substrate;

a hole structure extending from a first surface of the substrate to a second surface of the substrate;

oxic GST deposited in the hole structure; and

first and second electrodes located at opposing ends of the hole structure; wherein a diameter of the hole structure is less than about 5 nm to 100 nm and wherein the GST is deposited to a thickness of from 2-3 nm up to 50-100 nm, e.g., in a range of from 2 to 100 nm, a range of 3 to 50 nm, or other suitable range.

[0069] In one embodiment, the GST material of the disclosure is used to fabricate a memory cell structure in a substrate via, wherein surface of at least one of the electrodes bounding the via is

coated with a film of oxide GST material. The film of GST material can for example be from 4 nm to 50 nm in thickness. The via may have a diameter of 5 to 100 nm. The GST material may have an atomic weight ratio of about 2:2:5.

[0070] The oxide GST material more generally can be of any suitable type, as regards the stoichiometric or off-stoichiometric composition of such material. In some of the various embodiments contemplated by the present disclosure, the GST phase change material comprises from 5-60 atomic % Ge, from 1-80 atomic % Sb, and from 10-70 atomic % Te, with the atomic percentage amounts of such Ge, Sb and Te components totaling to 100 atomic %.

[0071] Among others of the various oxide GST materials contemplated by the disclosure for use in memory cell structures, GST materials can be used that have the formula $\text{Ge}_x\text{Sb}_y\text{Te}_z\text{A}_m$, in which A is one or more dopant species selected from the group consisting of N, C, In, Sn, and Se. The source of the elements N and C may be either the precursors of Ge, Sb, or Te, e.g., in organometallic precursors for such elements, in which the precursor includes a N- and/or C-containing moiety that serves to introduce nitrogen and/or carbon to the deposition for incorporation in the film being formed; alternatively, the source of the nitrogen and/or carbon can be additional precursors or added co-reactants. The nitrogen and/or carbon may be introduced to the deposition for incorporation in the film being formed, in a free form or in a bound, e.g., covalently bonded, form. As an example, the nitrogen component may be introduced to the deposition in free form, as nitrogen gas, or nitrogen can be introduced by addition of a nitrogenous component to the deposition, such as ammonia, urea, or other nitrogen-containing compound.

[0072] In $\text{Ge}_x\text{Sb}_y\text{Te}_z\text{A}_m$ films useful for such memory cell structures, x, y, z and m can have any suitable and compatible values. In various embodiments, x is about 0.05-0.6, y is about 0-0.8, z is about 0.1-0.7, and m is about 0-0.20. As mentioned, the dopant A can include more than one compatible dopant element from the group of dopant elements N, C, In, Sn, and Se, so that A_m comprises multiple A_m dopant elements. For example, the dopant elements can be carbon and nitrogen in the GST film, as respective A_m^1 and A_m^2 constituents of the aforementioned formula, wherein each of the A_m^1 and A_m^2 constituents is independently defined as to its amount in the GST alloy composition by m having a value of from 0 to 0.20.

[0073] In various preferred embodiments, the oxide GST alloy material used in the phase change memory structures of the present disclosure may be selected from among the following materials:

(i) material of the formula $\text{Ge}_x\text{Sb}_y\text{Te}_z\text{C}_m\text{N}_n$

wherein:

x is about 0.05-0.6, y is about 0-0.8, z is about 0.1-0.7, m is about 0.02-0.20, and n is about 0.02-0.20;

- (ii) material of the formula $\text{Ge}_x\text{Sb}_y\text{Te}_z\text{A}_m$, wherein A is a dopant element selected from the group of N, C, In, Sn, and Se, and wherein x is from 0.05 to 0.6, y is from 0 to 0.8, z is from 0.1 to 0.7, and m is from 0 to 0.20;
- (iii) material containing 27.5 to 33% germanium, with tellurium up to 55%, and the remainder being antimony;
- (iv) 225 GeSbTe doped with germanium to yield germanium-rich GeSbTe material;
- (v) germanium-enriched GeSbTe having a ratio of $\text{GeTe}:\text{Sb}_2\text{Te}_3$ that is in a range of from 3:1 to 10:1;
- (vi) GeSbTe material containing 25 to 60 % germanium, 8 to 25 % antimony, and 40 to 55% tellurium; and
- (vii) material selected from the group consisting of materials (ii)-(vi), as doped with at least one of carbon and nitrogen, wherein the amount of each is in a range of from 2 to 20 %.

[0074] The materials of the above-described type can include material in which $\text{Ge}_x\text{Sb}_y\text{Te}_z$ therein has an atomic composition selected from the group consisting of:

- (i) 22.5 at.% germanium, 22.5 at.% antimony and 55 at.% tellurium;
- (ii) 27.5 to 32.5 at.% germanium and from 50 to 55 at.% tellurium;
- (iii) 27 to 33% germanium, from 14 to 23% antimony and from 50 to 55% tellurium;
- (iv) 27.2% germanium, 18.2% antimony and 54.5% tellurium;
- (v) 30.7% germanium, 15.4% antimony, and 53.9% tellurium;
- (vi) 33.3% germanium, 13.3% antimony and 53.3% tellurium;
- (vii) 35.3% germanium, 11.8% antimony and 52.9% tellurium;
- (viii) 36% germanium, 14% antimony and 50% tellurium;
- (ix) 40% germanium, 8% antimony and 52% tellurium;
- (x)) 40% germanium, 5% antimony and 55% tellurium;
- (xi) 30% germanium, 19% antimony and 51% tellurium;
- (xii) 30% germanium, 16% antimony and 54% tellurium; and
- (xiii) 32% germanium, 14% antimony and 54% tellurium.

[0075] The GST alloy material when doped with carbon and/or nitrogen can be doped at any suitable dopant concentration levels. In various specific embodiments, the GST material can be doped with carbon at 2 to 20 at. %, or at 3 to 20 at. %, or at 2 to 15 at. %, or at 2 to 10 at. %, or at 3 to 10 at. %, or at 2 to 6 at. %. Likewise, the GST material can be doped with nitrogen at 2 to 20 at. %, or at 3 to 20 at. %, or at 3 to 15 at. %, or at 3 to 12 at. %, or at 3 to 10 at. %, or at 5 to 10 at. %. The specific dopant levels can be readily determined within the skill of the art, based on the present disclosure, by conducting doping at varying levels and characterizing the resulting doped GST films as to their characteristics and performance qualities.

[0076] Vapor deposition of the oxide GST material can be carried out by chemical vapor deposition (CVD) techniques, including for example atmospheric pressure CVD (APCVD), low

pressure CVD (LPCVD), ultrahigh vacuum CVD (UHVCVD), aerosol-assisted CVD (AACVD), digital CVD (DCVD), direct liquid injection CVD (DLICVD), microwave plasma-assisted CVD (MPCVD), plasma-enhanced CVD (PECVD), remote plasma-enhanced CVD (RPECVD), atomic layer CVD (ALCVD), hot wire CVD (HWCVD), metalorganic chemical vapor deposition (MOCVD), hybrid physical-chemical vapor deposition (HPCVD), rapid thermal CVD (RTCVD), and vapor phase epitaxy (VPE), using appropriately determined or selected CVD process parameters, e.g., as empirically determined by iterative multivariable change of process conditions, and characterization of the resulting GST films. Alternatively, the vapor deposition of the GST material can be carried out by atomic layer deposition (ALD) techniques, using ALD process parameters, e.g., pulse times, cycle durations, temperatures, pressures, volumetric flow rates, etc. that can be correspondingly determined by simple successive empirical runs in which process parameters are selectively varied to determine the best multivariable process envelope for conducting the ALD vapor deposition process to produce desired conformality of coating and character of resulting oxide GST films.

[0077] Oxygen incorporation in the film can as discussed above be effected in any suitable manner. In one preferred embodiment, oxygen gas in a concentration providing the desired oxygen incorporation in the deposited GST material is co-flowed in the precursor vapor mixture to the substrate in a deposition chamber for contacting with the substrate and resulting incorporation of the oxygen in the GST material. Oxygen doping, or diffusive penetration of oxygen into the deposited GST material after deposition is completed, or any other suitable oxygen incorporation process, can alternatively be employed. In the case of oxygen in-diffusion, the oxygen penetration may be due to the porous nature of the GST film and/or the existence of grain boundaries of the GST film. Such diffusion may be self-limited so that the percentage of oxygen incorporated in the GST film reaches an equilibrium level with a fixed composition.

[0078] In one embodiment, the disclosure relates to a GST phase change memory device, e.g., a GST PCRAM device, comprising an oxide GST material and having a reset current value below 1 mA, and preferably below 0.1 mA, e.g., in a range of from 0.05 to 0.4 mA, even when the device is as large in dimensions as 100 nm.

[0079] A further aspect the disclosure relates to a GST alloy having a reset speed of less than 50 ns and a reset current of less than 1.2 mA, preferably a reset current of less than 1.1 mA, and most preferably a reset current of less than 1.0 mA. Such GST alloys may be doped with one or more of carbon, nitrogen and oxygen. In specific embodiments of such GST alloys, the GST material may further contain 0.1-10% oxygen by weight, based on weight of the GST alloy, and optionally carbon and nitrogen. The disclosure therefore contemplates GST alloys having a low reset current and fast reset speed, as well as phase change memory device structures comprising such GST alloys.

[0080] Referring now to the drawings, FIG. 1 is a schematic representation of a GST device structure including an oxyc GST material of the present disclosure, in which the drawing includes the GST plug, a top electrode, and a bottom electrode, wherein the bottom or top electrode functions as a heater in the phase change memory device. The contact area of the heater to GST film determines the effective size of the device. The GST film can be isolated by etching to insulate the phase change memory cell in this area in relation to another one.

[0081] FIG. 2 is a schematic representation of an exemplary PCM GST device structure according to another embodiment of the present disclosure. In this structure, an oxyc GST alloy is deposited by metalorganic chemical vapor deposition (MOCVD) at a thickness in a range of 25 nanometers (nm) to 100 nm, in a pore having a depth on the order of 50 nm. The pore is formed by etching of the SiO₂ with a TiAlN layer constituting an etch stop layer. TiN then is deposited over the GST alloy, followed by patterning and etching of the TiN and GST to form an isolated PCM device. A layer of Ti may be deposited before TiN to enhance the adhesion of TiN to GST. Aluminum is deposited over the PCM structure and then pattern etched again to form an isolated Al pad over the TiN/GST stack. The Al pad is larger in the extent of its area than the TiN/GST stack, and thus part of the aluminum overlayer adheres to the SiO₂ layer to improve the seal of the sidewall of the GST and to afford protection of the GST element in the PCM device structure.

[0082] The characterization of the oxyc GST materials of the disclosure is more fully shown with reference to the data plotted in the graphs of FIGS. 3-10.

[0083] FIG. 3 is a graph showing oxygen and carbon concentration, in atomic percent, as a function of depth, in nanometers (nm) of an oxyc GST film according to one embodiment of the present disclosure, and germanium, antimony, tellurium and silicon concentrations, in arbitrary intensity units, as a function of depth of the GST film, in nanometers (nm). The oxygen level is <1 atomic %, e.g., between 0.1-1 atomic % of the GST film.

[0084] FIG. 4 is a graph showing oxygen and carbon concentration, in atomic percent, as a function of depth, in nanometers (nm) of an oxyc GST film according to another embodiment of the present disclosure, and germanium, antimony, tellurium and silicon concentrations, in atomic percent, as a function of depth of the GST film, in nanometers (nm). The oxygen level is between 1-10 atomic %. This is contrast to Fig.3 in which the oxygen is 5-10% less than that in Fig.4.

[0085] FIG. 5 is a graph of resistance, in ohms, as a function of reset current, in milliamps (mA), for an oxyc GST 225-based PCM device of the present disclosure, showing a dynamic range for the device of ~ 100 X, and a reset current of < 0.2mA. These data show that the oxyc GST material of the disclosure in a phase change memory device has a reset current of < 0.2mA, nearly 5 times smaller than a typical presently available 1mA reset current GST-based phase change memory device utilizing GST 225 alloy, but without the oxygen content of the oxyc GST material of the present disclosure.

[0086] FIG. 6 is a graph of reset current, in milliamperes (mA), as a function of voltage, in volts, for an oxide GST material of the present disclosure, wherein $V_t = 1.03$ volts, $V_h = 0.57$ volt, and $dV/dI = 3.31$ k Ω .

[0087] FIG. 7 is a graph of resistance, in ohms, as a function of reset current, in milliamperes (mA), for an oxide GST film-based PCM device of the present disclosure, showing curves for 0, 1, 2, 5, 10, 20, 50, 100, 200, 500 and 1000 cycles of phase change. The reset current is less than 0.1mA, 10 times smaller than the >1mA reset current of conventional devices of similar dimensions.

[0088] FIG. 8 is a graph of reset current, in milliamperes (mA), as a function of voltage, in volts, for an oxide GST material of the present disclosure, wherein $V_t = 0.98$ volts, $V_h = 0.59$ volt, and $dV/dI = 7.06$ k Ω .

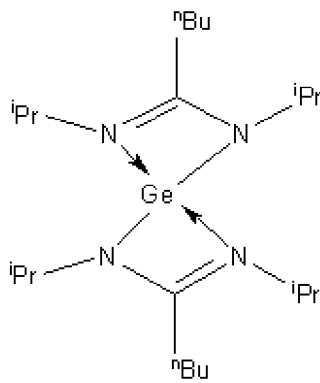
[0089] FIG. 9 is a graph of the parameters V_t (Δ), V_h ($\circ$), dV/dI , in k Ω ($\times$), Log R ($\diamond$), Log R in Ohms ($\square$), as a function of the number of phase change cycles, for an oxide GST material of the present disclosure.

[0090] FIG. 10 is a graph of resistance in ohms (Ω) for R_{set} ($\square$) and R_{reset} ($\diamond$), as a function of fall time, in nanoseconds, (ns), showing a $\frac{1}{2}$ full fall time set speed on the order of 250 nanoseconds, depending on the demarcation level.

[0091] It will therefore be appreciated that the oxide GST material of the present disclosure achieves superior properties for use in phase change memory devices, and that the oxide GST material of the present disclosure represents a substantial improvement in reset current characteristics, as compared to GST materials heretofore available in the art.

[0092] The disclosure in another aspect relates to a phase change memory device including an oxide GST material of the present disclosure operatively coupled with carbon nanotube electrode structures.

[0093] A still further aspect of the disclosure relates to GST phase change memory device structures. In various embodiments, the GST material in such phase change memory device structures comprises from 5-50 atomic % Ge, from 1-80 atomic % Sb, and from 10-70 atomic % Te, with the atomic percentage amounts of Ge, Sb, and Te totaling to 100 atomic %. In other embodiments, the GST material in the GST phase change memory device structure may be of the formula $Ge_xSb_yTe_zA_m$, in which A is one or more dopant species selected from the group consisting of N, C, In, Sn, and Se, wherein x is about 0.05-0.6, y is about 0-0.8, z is about 0.1-0.7, and m is about 0-0.20. These GST alloy materials can be formed by vapor deposition processes, e.g., MOCVD, using the following germanium, antimony and tellurium precursors:



SbTDMA

Te(tBu)₂

{nBuC(iPrN)₂}₂Ge,
also referred to as GeM

tris(dimethylamido)antimony

di-t-butyl telluride

or other suitable germanium, antimony and tellurium precursors.

[0094] A specific GST alloy of such type, which can advantageously be utilized in GST phase change memory device structures, is GST 24-19-58, i.e., Ge_{0.24}Sb_{0.19}Te_{0.58}. In a specific test of such material, a film of GST 24-19-58 was provided, which was 450 Å in thickness on a 135 nm PCM test device. Test data were gathered for such test device, and the data are shown in FIGS. 11 and 12.

[0095] FIG. 11 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} (◇), R_{set} (●) and R_{demarcation} (□).

[0096] FIG. 12 is a graph of cumulative probability (%) as a function of device set time, in nanoseconds (ns), for such GST alloy test device, with a vertical dashed line representation of the 50 ns set time. The data reflect a set speed of 30 ns ± 6 ns (1 sigma), substantially below the 50 ns reference set time.

[0097] Although the preceding discussion of the GST alloys of the present disclosure has been primarily directed to alloys characterized by low reset current (e.g., reset current below 1.2 mA, more preferably below 1.1 mA, and most preferably below 1 mA) for phase change memory device applications, the disclosure further contemplates the provision of GST alloys having fast reset speed, e.g., less than 50 ns for an illustrative 100 nm CD device, as well as having low reset current (e.g., reset current below 1.2 mA, more preferably below 1.1 mA, and most preferably below 1 mA). Such GST materials may be of any suitable composition described herein, such as a GST alloy that contains 0.1-10% oxygen by weight, based on weight of the GST alloy, in addition to carbon and nitrogen, or that otherwise comprises a GST alloy doped with one or more of carbon, nitrogen and oxygen. Preferred fast reset speed/low reset current materials of the disclosure have a reset speed of less than 50 ns, and a reset current of less than 1 mA.

[0098] FIG. 13 is a graph of V (volts), dV/dI (Kohms) and I_{rs,sat} (mA), and read resistance (ohms), as a function of number of cycles, showing the results of a cycle endurance test for the same GST 24-19-58, i.e., Ge_{0.24}Sb_{0.19}Te_{0.58} alloy material that was used to generate the data of

FIGS. 11 and 12. The test used the square pulse method with a reset pulse time of 50ns and set pulse time of 50ns. The data are shown in the graph for V_t (Δ), V_h (x), dV/dI ($\times$), $I_{rs,sat}$ ($\bullet$), Set R ($\blacklozenge$), and Reset R ($\blacksquare$). More than 1×10^8 cycles were completed with a stable R_{reset} , R_{set} , V_t , V_h , and dV/dI before the device failed stuck-Reset.

[0099] FIG. 14 is a graph of V (volts), dV/dI (Kohms) and $I_{rs,sat}$ (mA), and read resistance (ohms), as a function of number of cycles, showing the results of a corresponding cycle endurance test for the same GST 24-19-58, i.e., $Ge_{0.24}Sb_{0.19}Te_{0.58}$ alloy material that was used to generate the data of FIG. 13. The test used the square pulse method with a reset pulse time of 50ns and set pulse time of 50ns. The data are shown in the graph for V_t (Δ), V_h (x), dV/dI , in $k\Omega$ ($\times$), $I_{rs,sat}$, in milliamps ($\bullet$), Set R ($\blacklozenge$), and Reset R ($\blacksquare$). The data shown in FIG. 14 are direct pulse results that were generated without using a quench circuit. More than 1×10^9 cycles were completed, as shown by the respective curves for which data are presented.

[00100] In the vapor deposition of GST materials on substrates, physical vapor deposition (PVD) techniques have been utilized widely for forming GST alloys in the manufacture of phase change memory devices. Nonetheless, metalorganic chemical vapor deposition (MOCVD) can be utilized to achieve substantially improved GST alloy material properties, in relation to PVD alloys, for high speed and low reset current applications. Conformal MOCVD processes must be used if GST alloys are to be void-free fill confined structures at the 20nm node and beyond. MOCVD processes thus are usefully employed to deposit GST alloys in confined device structures, and such processes when optimized in specific chemical vapor deposition systems enable conformal deposition to fill < 15 nm confined structures, e.g., trench and hole structures.

[00101] Compared to PCM devices made from PVD GST alloys, devices fabricated using MOCVD GST alloys and processes of the present disclosure have been shown to achieve a fourfold improvement in device speed, with set time < 50 ns in ~100 nm size devices, e.g., faster than 15 ns in ~135 nm size large PCM devices. Such set time is 3-4 times faster than typical 150-20 ns set time exhibited by devices of similar size made from these PVD $Ge_2Sb_2Te_5$ alloys. Devices made from these fast speed MOCVD GST alloys also exhibit a twofold reduction in reset current, in relation to PCM devices made with PVD GST alloys, e.g., $Ge_2Sb_2Te_5$, as well as cycle endurance of greater than 1×10^8 time at 50 ns set time.

[00102] In an illustrative MOCVD GST process, which may be usefully employed for forming MOCVD GST alloy compositions in accordance with the present disclosure, the aforementioned precursors, $\{nBuC(iPrN)_2\}_2Ge$, tris(dimethylamido)antimony, and di-t-butyl telluride, are utilized as germanium, antimony and tellurium source reagents, respectively.

[00103] The corresponding process for forming a germanium antimony telluride material on a substrate may be carried out, as comprising: vaporizing germanium, antimony and tellurium precursors for the germanium antimony telluride material, to form corresponding precursor vapor, with such precursors comprising $Ge[Pr^iNC(n-Bu)NPr^i]_2$ as the germanium precursor,

tris(dimethylamido)antimony as the antimony precursor, and $\text{Te}(\text{tBu})_2$ as the tellurium precursor; heating the tellurium precursor vapor to temperature in a range of from 180°C to 450°C for activation thereof, separate from the other precursors; contacting germanium precursor vapor, antimony precursor vapor, and activated tellurium precursor vapor with the substrate under conditions enabling formation of the germanium antimony telluride material on the substrate, wherein the substrate during such contacting is at temperature in a range of from 110°C to 300°C.

[00104] In specific embodiments of such process, the tellurium precursor vapor may be heated in the heating operation to temperature in a range of from 200°C to 320°C, e.g., a temperature of 300°C. In preferred implementations, the contacting of the germanium precursor vapor, antimony precursor vapor, and activated tellurium precursor vapor with the substrate is carried out in a deposition chamber, and the activation heating of the tellurium precursor vapor is carried out in an activation zone upstream of the deposition chamber.

[00105] FIG. 15(a) is a cross-sectional scanning electron micrograph (SEM) image of an MOCVD GST alloy filling a hole of 15 nm size, and FIG. 15(b) is a cross-sectional scanning electron micrograph (SEM) image of an MOCVD GST alloy filling a hole of ~20 nm size, as deposited by the above-described GST material formation process. As shown by the SEM image, the MOCVD GST alloy provides good conformal coverage in the hole.

[00106] Any suitable GST alloy compositions may be employed for such confined device structure deposition applications. In various embodiments, the alloy is a 325 GST alloy, $\text{Ge}_{0.3}\text{Sb}_{0.2}\text{Te}_{0.5}$. In other embodiments, the alloy is a 415 GST alloy, $\text{Ge}_{0.4}\text{Sb}_{0.1}\text{Te}_{0.5}$.

[00107] FIG. 16(a) is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$), R_{set} ($\bullet$) and $R_{\text{demarcation}}$ (—), in a 135 nm device. This graph provides a set speed test curve showing that a phase change memory device made with MOCVD GST alloy takes less than 30 ns for resistance to reach ~ 10 kilo-ohms ($\text{k}\Omega$) set resistance level from a reset resistance level of ~500 $\text{k}\Omega$ as shown by the demarcation line. FIG. 16(b) is a speed test curve showing a phase change memory made with MOCVD GST taking only ~12 ns to reach ~20 $\text{k}\Omega$ set resistance level from reset resistance level of ~1M Ω . FIG. 16(c) shows cycle endurance of such MOCVD GST material as measured at 50 ns set time. The MOCVD GST alloy composition for which data are shown in FIG. 16(a)-(c) was a 24-18-58 GST composition, $\text{Ge}_{0.24}\text{Sb}_{0.18}\text{Te}_{0.58}$.

[00108] In another embodiment, a 36-14-50 GST alloy composition of the disclosure exhibited 20 ns set and 30 ns reset time in duration tests to nearly $1\text{e}9$ cycles.

[00109] Although the disclosure herein is primarily directed to MOCVD formation of GST films, it will be appreciated that other vapor deposition techniques can be usefully employed in the broad practice of the present disclosure, including chemical vapor deposition, atomic layer deposition, etc. The GST alloy compositions and deposition techniques of the present disclosure are effective to provide void-free fills in confined device structures.

[00110] The disclosure in another aspect relates to porous GST material that is doped or oxidized by oxygen, to lower resistivity after phase change of the material, and to lower phase change temperature for the material. In general, MOCVD GST materials that contain high levels of carbon characteristically have high resistivity after annealing, e.g., resistivity levels on the order of 0.1 ohm-centimeters (Ω -cm), which render such materials unsuitable for phase change memory applications, in which resistivity values of 0.01 Ω -cm or less are desired. Oxygen-doped GST, however, is able to achieve such low resistivity, e.g., 0.01 Ω -cm, after annealing at significantly lower temperatures than are typically employed for GST materials lacking oxygen doping or oxidized character. For example, in some instances, only 300°C annealing is required to achieve resistivity levels of 0.01 Ω -cm or less, as opposed to temperatures of 350°C or higher otherwise required for such annealing to obtain suitable resistivity.

[00111] Accordingly, GST doping or oxidation by oxygen enables low resistivity and low annealing temperature to be achieved, which in turn allow fast transient memory switching with low reset current requirement.

[00112] Such GST doping or oxidation by oxygen involves processing of GST in such manner that the GST material is a low density film, which allows infusion of oxygen into the film, e.g., from a deposition ambient when such deposition ambient in the vapor deposition chamber contains oxygen. Alternatively, oxygen may be incorporated in the film by placement of the low-density film in a chamber that is filled with oxygen gas. In still other cases, oxygen may be incorporated in the GST film by exposing the low-density GST film to ambient air. Oxygen incorporation can also be effected in the GST film by introducing oxygen in one or more of the precursor vapor streams or in co-reactive gas that is introduced to the deposition chamber in the formation of the GST film.

[00113] It will be appreciated that the GST film can be formed in any suitable manner to incorporate oxygen therein, and for such purpose the process conditions for the GST film deposition can be appropriately varied to yield low-density GST films, within the skill of the art, based on the disclosure herein.

[00114] FIG. 17 is a graph of resistivity, in Ω -cm, as a function of annealing temperature, in degrees Centigrade, for illustrative oxygen-containing porous GST films whose micrographs are shown in FIGS. 18-21.

[00115] FIG. 18 is a micrograph of a porous GST film, which as grown had a resistivity value greater than 32 Ω -cm. Such film had a 350 Å thickness. FIG. 19 is a SEM micrograph of a corresponding oxygen-containing porous GST film after annealing at 300°C, as a result of which the film had a resistivity of 0.018 ± 0.0014 Ω -cm. FIG. 20 is a SEM micrograph of a corresponding oxygen-containing porous GST film after annealing at 350°C, in consequence of which the film had a resistivity of 0.00352 ± 0.00006 Ω -cm. FIG. 21 is a SEM micrograph of a corresponding oxygen-containing porous GST film after annealing at 375°C, which resulted in the

film having a resistivity of $0.00238 \pm 0.00036 \text{ } \Omega\text{-cm}$, albeit with a less desirable morphology, as compared with films annealed at lower temperatures.

[00116] Accordingly, these resistivity values and associated temperatures suggest that porous GST films are advantageously subjected to oxidic annealing (either by annealing in an oxygen-containing ambient, or by annealing a porous GST film already containing oxygen from prior processing) at temperature not exceeding 350°C , e.g., temperature in a range of from 300°C to 350°C .

[00117] GST films containing oxygen thus enable significantly faster PCM devices to be achieved, with significantly lowered resistivity after annealing. For example, GST film compositions of 415, 325 and 225 GST alloys can attain set speeds $< 100 \text{ ns}$ in films containing 1-2% oxygen, in addition to containing carbon and nitrogen. Such discovery is at odds with the conventional wisdom in the phase change memory field, according to which oxygen has been regarded as a deleterious impurity in GST films. The present discovery that very fast speed devices can be fabricated from GST films containing oxygen, contrary to such conventional wisdom, is not fully understood.

[00118] Nonetheless, without wishing to be bound by any hypothesis or speculated mechanism, it may be that oxygen incorporated in the GST film after deposition introduces film defects in the GST morphology, so that the phase change from an amorphous state to crystalline state may be significantly faster due to easier movement of atoms during the phase change in the low-density film. Alternatively, it may be that oxygen incorporated during deposition from residual oxygen in the chamber during deposition introduces defects in the GST film morphology that increase the number of nucleation centers in the material, in combination with existing carbon and nitrogen impurities that may be present in the film.

[00119] As discussed above, the presence of oxygen in the GST film also is beneficial in achieving low resistivity after annealing at temperatures as low as 300°C , enabling resistivities to be $< 0.01 \text{ } \Omega\text{-cm}$. In this respect, it has been determined that prolonged oxidic film annealing, e.g., at temperature of at least 300°C for a time of from 2 to 24 hours, achieves high-speed, low resistivity GST films. Again, while the mechanism of operation is not yet fully elucidated, it may be that such prolonged annealing promotes the formation of additional nucleation centers that in turn enable faster crystallization during phase change operation.

[00120] FIG. 22 is a graph of oxygen and carbon concentration, in atomic percent, and germanium, tellurium, antimony, and silicon intensity, in arbitrary units, as a function of material depth in the GST material, for an MOCVD GST 225 alloy containing $\sim 1\text{-}2\%$ oxygen.

[00121] FIG. 23 is a graph of oxygen and carbon concentration, in atomic percent, and germanium, tellurium, antimony, and silicon intensity, in arbitrary units, as a function of material depth in the GST material, for an MOCVD GST 325 alloy containing $\sim 1\text{-}2\%$ oxygen.

[00122] FIG. 24 is a graph of resistivity, in Ω -cm, as a function of annealing temperature, in degrees Centigrade, for oxide GST 225, GST 325, and GST 415 alloys, showing that the low resistivities were obtained in such oxide alloys by annealing at temperature in a range of from 300 to 400°C.

[00123] FIG. 25 is a graph of oxygen and carbon concentration, in atomic percent, and germanium, tellurium, antimony, and silicon intensity, in arbitrary units, as a function of material depth in the GST material, for an MOCVD GST 415 alloy containing ~ 1- 10% oxygen.

[00124] FIG. 26 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$) and R_{set} ($\bullet$) in a 112 nm device after annealing of a GST material having an 86 ns set speed, at 375°C for 24 hours in argon gas. FIG. 27 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$), R_{set} ($\bullet$) and $R_{\text{demarcation}}$ (—) (ohms), in a 135 nm device after annealing of an oxide GST material having a 55 ns set speed, at 375°C for 24 hours in argon gas. The results show that the ~100 nm size device utilizing an oxide GST 225 composition achieved 20-30 ns set speed after 375°C annealing for 24 hours in argon gas.

[00125] FIG. 28 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$) and R_{set} ($\bullet$) in a 112 nm device after annealing of a 325 GST material having a 215 ns set speed, at 375°C for 24 hours in argon gas. FIG. 29 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$), R_{set} ($\bullet$) and $R_{\text{demarcation}}$ (—) (ohms), in a 135 nm device after annealing of an oxide 325 GST material having a 111 ns set speed, at 375°C for 24 hours in argon gas. The results show that the ~100 nm size device utilizing an oxide GST 325 composition achieved 20-30 ns set speed after 375°C annealing for 24 hours in argon gas.

[00126] FIG. 30 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$) and R_{set} ($\bullet$) in an ~100 nm device including a 415 GST material having an ~80 ns set speed.

[00127] FIG. 31 is a graph of read resistance, in ohms (Ω), as a function of square SET pulse width(s), for R_{reset} ($\diamond$), R_{set} ($\bullet$) and $R_{\text{demarcation}}$ (—) (ohms), in an ~ 100 nm device after annealing of a 415 GST material at 375°C for 24 hours in argon gas. The results show that the ~100 nm size device utilizing a GST 415 composition achieved 20-30 ns set speed after 375°C annealing for 24 hours in argon gas.

[00128] Accordingly, the present disclosure in one aspect contemplates a GST phase change memory device, comprising a hole or trench structure having a size dimension below 15 nm, with an oxygen-containing GST material therein having a set time of less than 15 ns. The GST material in such device may comprise a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy. Alternatively, such GST material may comprise a 24-18-58 GST composition. In such GST phase change memory device, the GST material may have a resistivity of less than 0.01 Ω -cm.

[00129] The disclosure in another aspect contemplates a GST phase change memory device, comprising a hole or trench structure having a size dimension below 15 nm with an oxygen-containing GST material therein having a set speed of less than 100 ns. The set speed and such device may be less than 30 ns. The GST material can comprise a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy. Alternatively, the GST material can comprise a 24-18-58 GST composition. The GST material in such device may have a resistivity of less than 0.01 Ω -cm.

[00130] The disclosure in other embodiments contemplates (i) GST alloys with compositions between 225-325, which have been demonstrated to achieve $1e8$ cycle endurance at 50 ns set time, and (ii) GST alloys with compositions between 325-415, which have been tested, and achieved $1e9$ cycle endurance at 20 ns set time.

[00131] In another embodiment, the disclosure relates to a 36-14-50 GST alloy composition. Such composition has been demonstrated to exhibit 20 ns set and 30 ns reset time in duration tests to nearly $1e9$ cycles. Such composition may be an oxyc composition.

[00132] The disclosure relates in another aspect to an oxygen-containing GST material having a set time of less than 15 ns. The GST material may comprise a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy. Alternatively, the GST material may comprise a 24-18-58 GST composition. The GST material may have a resistivity of less than 0.01 Ω -cm.

[00133] In a further aspect, the disclosure relates to an oxygen-containing GST material having a set speed of less than 100 ns. The GST material may have a set speed of less than 30 ns. The GST material may comprise a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy. Alternatively, the GST material may comprise a 24-18-58 GST composition. The GST material may have a resistivity of less than 0.01 Ω -cm.

[00134] A further aspect the disclosure relates to a GST material having a set time of less than 15 ns, a set speed of less than 100 ns, and a resistivity of less than 0.01 Ω -cm. The GST material may comprise a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy. Alternatively, the GST material may comprise a 24-18-58 GST composition.

[00135] Yet another aspect of the disclosure relates to a GST material having a programming cycle endurance greater than 5×10^8 , a set time of 20ns or less, and <20ns set speed. Another aspect of the disclosure relates to a GST PCM device comprising such a GST material. The device may for example be a 100 nm-scale PCM device. The GST material may comprise a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy. Alternatively, the GST material may comprise a 24-18-58 GST composition. The GST material can be formed by CVD, MOCVD, or ALD, or other vapor deposition method. The GST material can be formed by a process including: vaporizing germanium, antimony and tellurium precursors for the germanium antimony telluride material, to form corresponding precursor vapor, with such precursors comprising $\text{Ge}[\text{Pr}^i\text{NC}(\text{n-Bu})\text{NPr}^j]_2$ as the germanium precursor, tris(dimethylamido)antimony as the antimony precursor, and $\text{Te}(\text{tBu})_2$ as the tellurium precursor; heating the tellurium precursor vapor to temperature in a range of from

180°C to 450°C for activation thereof, separate from the other precursors; contacting germanium precursor vapor, antimony precursor vapor, and activated tellurium precursor vapor with a substrate under conditions enabling formation of the germanium antimony telluride material on the substrate, wherein the substrate during such contacting is at temperature in a range of from 110°C to 300°C. The GST material may have oxygen incorporated therein during such process or subsequent thereto. The GST material having oxygen incorporated therein, may be annealed at temperature in a range of from 300°C to 375°C for a period of from 2 to 24 hours. The PCM device comprising such GST material may have a confined structure containing the GST material, with the confined structure having a characteristic dimension, e.g., transverse dimension or diameter, that is less than 20 nm, or less than 15 nm. The confined structure may be a trench or hole structure.

[00136] In a further aspect, the disclosure relates to a method of making a GST film having resistivity below 0.01 Ω -cm, said method comprising incorporating oxygen in said GST film during or after vapor deposition formation thereof, and annealing said GST film having oxygen incorporated therein, at temperature in a range of from 300°C to 375°C for a period of from 2 to 24 hours. The temperature range in a specific embodiment may be in a range of from 300°C to 350°C. The annealing may be carried out in an inert gas atmosphere.

[00137] Another aspect the disclosure relates to a GST material having at least one of the characteristics of: a set time of less than 15 ns; a set speed of less than 100 ns; and a resistivity of less than 0.01 Ω -cm, wherein said GST material has been formed by a process comprising: vaporizing germanium, antimony and tellurium precursors for the germanium antimony telluride material, to form corresponding precursor vapor, with such precursors comprising $\text{Ge}[\text{Pr}^i\text{NC}(\text{n-Bu})\text{NPr}^i]_2$ as the germanium precursor, tris(dimethylamido)antimony as the antimony precursor, and $\text{Te}(\text{tBu})_2$ as the tellurium precursor; heating the tellurium precursor vapor to temperature in a range of from 180°C to 450°C for activation thereof, separate from the other precursors; contacting germanium precursor vapor, antimony precursor vapor, and activated tellurium precursor vapor with a substrate under conditions enabling formation of the germanium antimony telluride material on the substrate, wherein the substrate during such contacting is at temperature in a range of from 110°C to 300°C. Such GST material can be manufactured, wherein oxygen has been incorporated therein during said process or subsequent thereto. The GST material corresponding early having oxygen incorporated therein can be processed by annealing at temperature in a range of from 300°C to 375°C for a period of from 2 to 24 hours.

[00138] It will be appreciated that GST materials within the scope of the present disclosure may be formed by vapor deposition techniques in a wide variety of process variations, and subsequently processed by correspondingly variant techniques, to produce GST materials of desired character, having suitability for phase change memory applications as well as other uses and applications.

[00139] Thus, while the disclosure has been set forth herein in reference to specific aspects, features and illustrative embodiments, it will be appreciated that the utility of the disclosure is not thus limited, but rather extends to and encompasses numerous other variations, modifications and alternative embodiments, as will suggest themselves to those of ordinary skill in the field of the present disclosure, based on the description herein. Correspondingly, the invention as hereinafter claimed is intended to be broadly construed and interpreted, as including all such variations, modifications and alternative embodiments, within its spirit and scope.

THE CLAIMS

What is claimed is:

1. A GST material selected from among:

- (a) GST materials having oxygen incorporated therein at concentration of from 0.10 to 10 atomic % of the GST material; and
- (b) GST materials having a reset current of less than 0.1 milliamps when the GST material is comprised in a GST phase change random access memory device.
- (c) GST materials containing 1-3 atomic % oxygen, and having reset current below 0.1 mA when disposed in a PCRAM device;
- (d) oxo GST materials having a reset current below 1 mA;
- (e) GST materials having a reset speed of less than 50 ns and a reset current of less than 1.2 mA;
- (f) oxygen-containing GST materials having a set time of less than 15 ns;
- (g) oxygen-containing GST materials having a set speed of less than 100 ns;
- (h) GST materials having a set time of less than 15 ns, a set speed of less than 100 ns, and a resistivity of less than 0.01 Ω ;
- (i) GST materials having a 36-14-50 GST alloy composition; and
- (j) GST materials having a programming cycle endurance greater than 5×10^8 , a set time of 20 ns or less, and < 20 ns set speed.

2. A GST material selected from among:

- (a) GST materials having oxygen incorporated therein at concentration of from 0.10 to 10 atomic % of the GST material; and
- (b) GST materials having a reset current of less than 0.1 milliamps when the GST material is comprised in a GST phase change random access memory device.

3. The GST material of claim 2, having oxygen incorporated therein at concentration of from 0.10 to 10 atomic % of the GST material.

4. The GST material of claim 2, containing 1-3 atomic % oxygen.

5. The GST material of claim 4, having reset current below 0.1 mA in a PCRAM device.

6. The GST material of claim 2, having a reset current of less than 0.1 milliamps when the GST material is comprised in a GST phase change random access memory device.

7. The GST material of claim 6, having a reset current value of from 0.01 to 0.09 mA.
8. The GST material of claim 6, having a reset current value of from 0.01 to 0.07 mA.
9. The GST material of claim 6, having a reset current value of from 0.01 to 0.05 mA.
10. The GST material of claim 6, having a reset current value of from 0.05 to 0.09 mA.
11. The GST material of claim 2, having an atomic weight ratio of G:S:T of about 2:2:5.
12. The GST material of claim 2, comprising from 5-50 atomic % Ge, from 1-80 atomic % Sb, and from 10-70 atomic % Te, with the atomic percentage amounts of Ge, Sb and Te totaling to 100 atomic %.
13. The GST material of claim 2, of the formula $\text{Ge}_x\text{Sb}_y\text{Te}_z\text{A}_m$, in which A is one or more dopant species selected from the group consisting of N, C, In, Sn, and Se, wherein x is about 0.05-0.6, y is about 0-0.8, z is about 0.1-0.7, and m is about 0-0.20.
14. The GST material of claim 2, selected from the group consisting of compositions of the formulae:
 - (i) material of the formula $\text{Ge}_x\text{Sb}_y\text{Te}_z\text{C}_m\text{N}_n$ wherein:
x is about 0.05-0.6, y is about 0-0.8, z is about 0.1-0.7, m is about 0.02-0.20, and n is about 0.02-0.20;
 - (ii) material of the formula $\text{Ge}_x\text{Sb}_y\text{Te}_z\text{A}_m$, wherein A is a dopant element selected from the group of N, C, In, Sn, and Se, and wherein x is from 0.05 to 0.6, y is from 0 to 0.8, z is from 0.2 to 0.7, and m is from 0 to 0.15;
 - (iii) material containing 27.5 to 33% germanium, with tellurium up to 55%, and the remainder being antimony;
 - (iv) 225 GeSbTe doped with germanium to yield germanium-rich GeSbTe material;
 - (v) germanium-enriched GeSbTe having a ratio of $\text{GeTe}:\text{Sb}_2\text{Te}_3$ that is in a range of from 3:1 to 10:1;
 - (vi) GeSbTe material containing 25 to 60 % germanium, 8 to 25 % antimony, and 40 to 55% tellurium; and
 - (vii) material selected from the group consisting of materials (ii)-(vi), as doped with at least one of carbon and nitrogen, wherein the amount of each is in a range of from 2 to 20 %.

15. The GST material of claim 2, including an atomic composition GeSbTe selected from the group consisting of:

- (i) 22.5 at.% germanium, 22.5 at.% antimony and 55 at.% tellurium;
- (ii) 27.5 to 32.5 at.% germanium and from 50 to 55 at.% tellurium;
- (iii) 27 to 33% germanium, from 14 to 23% antimony and from 50 to 55% tellurium;
- (iv) 27.2% germanium, 18.2% antimony and 54.5% tellurium;
- (v) 30.7% germanium, 15.4% antimony, and 53.9% tellurium;
- (vi) 33.3% germanium, 13.3% antimony and 53.3% tellurium;
- (vii) 35.3% germanium, 11.8% antimony and 52.9% tellurium;
- (viii) 36% germanium, 14% antimony and 50% tellurium;
- (ix) 40% germanium, 8% antimony and 52% tellurium;
- (x)) 40% germanium, 5% antimony and 55% tellurium;
- (xi) 30% germanium, 19% antimony and 51% tellurium;
- (xii) 30% germanium, 16% antimony and 54% tellurium; and
- (xiii) 32% germanium, 14% antimony and 54% tellurium.

16. A GST material containing 1-3 atomic % oxygen, and having reset current below 0.1 mA in a PCRAM device.

17. A method of making a phase change material, comprising forming a germanium-antimony-tellurium (GST) material, and incorporating oxygen therein at concentration of from 0.10 to 10 atomic %, based on atomic weight of the GST material.

18. The method of claim 17, wherein the GST material is formed by vapor deposition of germanium, antimony and tellurium.

19. The method of claim 17, wherein the GST material is formed by vapor deposition of germanium, antimony and tellurium from precursors comprising $\{n\text{BuC}(\text{iPrN})_2\}_2\text{Ge}$, tris(dimethylamido)antimony and di-t-butyl telluride.

20. The method of claim 19, wherein the vapor deposition comprises chemical vapor deposition.

21. The method of claim 19, wherein the vapor deposition comprises atomic layer deposition.

22. The method of claim 17, wherein oxygen is incorporated in the GST material from an oxygen source comprising oxygen, ozone or singlet oxygen.

23. The method of claim 22, wherein oxygen is incorporated in the GST material during forming of the GST material.
24. The method of claim 22, wherein oxygen is incorporated in the GST material after forming of the GST material.
25. A method of making a phase change material, comprising forming a germanium-antimony-tellurium (GST) material, and incorporating oxygen therein at sufficient concentration to yield a reset current of less than 0.1 milliamps when the GST material is comprised in a GST phase change random access memory device
26. A phase change memory device, comprising: a substrate; a hole structure extending from a first surface of the substrate to a second surface of the substrate; GST material of any one of claims 2 to 16, deposited in the hole structure; and first and second electrodes located at opposing ends of the hole structure.
27. A GST phase change memory device, comprising an oxyc GST material and having a reset current value below 1 mA.
28. The GST phase change memory device of claim 27, having a reset current value in a range of from 0.05 to 0.4 mA.
29. A GST alloy having a reset speed of less than 50 ns and a reset current of less than 1.2 mA.
30. The GST alloy of claim 29, doped with one or more of carbon, nitrogen and oxygen.
31. The GST alloy of claim 29, containing 0.1-10% oxygen by weight, based on weight of the GST alloy.
32. The GST alloy of claim 31, further comprising carbon and nitrogen.
33. The GST alloy of claim 29, having a reset current of less than 1.1 mA.
34. The GST alloy of claim 29, having a reset current of less than 1.0 mA.

35. A GST phase change memory device, comprising a hole structure having a size dimension below 15 nm, with an oxygen-containing GST material therein having a set time of less than 15 ns.
36. The GST phase change memory device of claim 35, wherein said GST material comprises a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy.
37. The GST phase change memory device of claim 35, wherein said GST material comprises a 24-18-58 GST composition.
38. The GST phase change memory device of claim 35, wherein said GST material has a resistivity of less than 0.01 Ω -cm.
39. A GST phase change memory device, comprising a hole structure having a size dimension below 15 nm with an oxygen-containing GST material therein having a set speed of less than 100 ns.
40. The GST phase change memory device of claim 39, wherein the set speed is less than 30 ns.
41. The GST phase change memory device of claim 39, wherein said GST material comprises a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy.
42. The GST phase change memory device of claim 39, wherein said GST material comprises a 24-18-58 GST composition.
43. The GST phase change memory device of claim 39, wherein said GST material has a resistivity of less than 0.01 Ω -cm.
44. An oxygen-containing GST material having a set time of less than 15 ns.
45. The GST material of claim 44, comprising a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy.
46. The GST material of claim 44, comprising a 24-18-58 GST composition.
47. The GST material of claim 44, having a resistivity of less than 0.01 Ω -cm.
48. An oxygen-containing GST material having a set speed of less than 100 ns.

49. The GST material of claim 48, wherein the set speed is less than 30 ns.
50. The GST material of claim 48, comprising a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy.
51. The GST material of claim 48, comprising a 24-18-58 GST composition.
52. The GST material of claim 48, having a resistivity of less than 0.01 Ω -cm.
53. A GST material having a set time of less than 15 ns, a set speed of less than 100 ns, and a resistivity of less than 0.01 Ω -cm.
54. The GST material of claim 53, comprising a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy.
55. The GST material of claim 53, comprising a 24-18-58 GST composition.
56. A method of making a GST film having resistivity below 0.01 Ω -cm, said method comprising incorporating oxygen in said GST film during or after vapor deposition formation thereof, and annealing said GST film having oxygen incorporated therein, at temperature in a range of from 300°C to 375°C for a period of from 2 to 24 hours.
57. The method of claim 56, wherein the temperature is in a range of from 300°C to 350°C.
58. The method of claim 56, wherein the annealing is carried out in an inert gas atmosphere.
59. A GST material having at least one of the characteristics of: a set time of less than 15 ns; a set speed of less than 100 ns; and a resistivity of less than 0.01 Ω -cm, wherein said GST material has been formed by a process comprising: vaporizing germanium, antimony and tellurium precursors for the germanium antimony telluride material, to form corresponding precursor vapor, with such precursors comprising $\text{Ge}[\text{Pr}^i\text{NC}(\text{n-Bu})\text{NPr}^i]_2$ as the germanium precursor, tris(dimethylamido)antimony as the antimony precursor, and $\text{Te}(\text{tBu})_2$ as the tellurium precursor; heating the tellurium precursor vapor to temperature in a range of from 180°C to 450°C for activation thereof, separate from the other precursors; contacting germanium precursor vapor, antimony precursor vapor, and activated tellurium precursor vapor with a substrate under

conditions enabling formation of the germanium antimony telluride material on the substrate, wherein the substrate during such contacting is at temperature in a range of from 110°C to 300°C.

60. The GST material of claim 59, wherein oxygen has been incorporated therein during said process or subsequent thereto.

61. The GST material of claim 60, wherein the GST material having oxygen incorporated therein, has been annealed at temperature in a range of from 300°C to 375°C for a period of from 2 to 24 hours.

62. A GST material having a 36-14-50 GST alloy composition.

63. The GST material of claim 62, having a 20 ns set time and a 30 ns reset time.

64. The GST material of claim 62, having an oxyc GST composition.

65. A GST material having a programming cycle endurance greater than 5×10^8 , a set time of 20ns or less, and <20ns set speed.

66. The GST material of claim 65, comprising a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy.

67. The GST material of claim 65, comprising a 24-18-58 GST composition.

68. The GST material of claim 65, formed by CVD, MOCVD or ALD.

69. The GST material of claim 65, formed by a process comprising: vaporizing germanium, antimony and tellurium precursors for the germanium antimony telluride material, to form corresponding precursor vapor, with such precursors comprising $\text{Ge}[\text{Pr}^i\text{NC}(\text{n-Bu})\text{NPr}^i]_2$ as the germanium precursor, tris(dimethylamido)antimony as the antimony precursor, and $\text{Te}(\text{tBu})_2$ as the tellurium precursor; heating the tellurium precursor vapor to temperature in a range of from 180°C to 450°C for activation thereof, separate from the other precursors; contacting germanium precursor vapor, antimony precursor vapor, and activated tellurium precursor vapor with a substrate under conditions enabling formation of the germanium antimony telluride material on the substrate, wherein the substrate during such contacting is at temperature in a range of from 110°C to 300°C.

70. The GST material of claim 69, wherein oxygen has been incorporated therein during said process or subsequent thereto.

71. The GST material of claim 70, wherein the GST material having oxygen incorporated therein, has been annealed at temperature in a range of from 300°C to 375°C for a period of from 2 to 24 hours.

72. A GST PCM device comprising a GST material according to claim 65.

73. The GST PCM device of claim 72, wherein the GST material is in a confined structure having a transverse dimension of less than 20 nm.

74. The GST PCM device of claim 73, wherein said transverse dimension is less than 15 nm.

75. The GST PCM device of claim 74, wherein said confined structure is a trench or hole structure.

76. The GST PCM device of claim 72, wherein the GST material comprises a 325 GST alloy, a 415 GST alloy, or a 225 GST alloy.

77. The GST PCM device of claim 72, wherein the GST material comprises a 24-18-58 GST composition.

78. The GST PCM device of claim 72, wherein the GST material is formed by CVD, MOCVD or ALD.

79. The GST PCM device of claim 72, wherein the GST material formed by a process comprising: vaporizing germanium, antimony and tellurium precursors for the germanium antimony telluride material, to form corresponding precursor vapor, with such precursors comprising $\text{Ge}[\text{Pr}^i\text{NC}(\text{n-Bu})\text{NPr}^i]_2$ as the germanium precursor, tris(dimethylamido)antimony as the antimony precursor, and $\text{Te}(\text{tBu})_2$ as the tellurium precursor; heating the tellurium precursor vapor to temperature in a range of from 180°C to 450°C for activation thereof, separate from the other precursors; contacting germanium precursor vapor, antimony precursor vapor, and activated tellurium precursor vapor with a substrate under conditions enabling formation of the germanium antimony telluride material on the substrate, wherein the substrate during such contacting is at temperature in a range of from 110°C to 300°C.

80. The GST PCM device of claim 79, wherein oxygen has been incorporated in the GST material during said process or subsequent thereto.

81. The GST PCM device of claim 80, wherein the GST material having oxygen incorporated therein, has been annealed at temperature in a range of from 300°C to 375°C for a period of from 2 to 24 hours.

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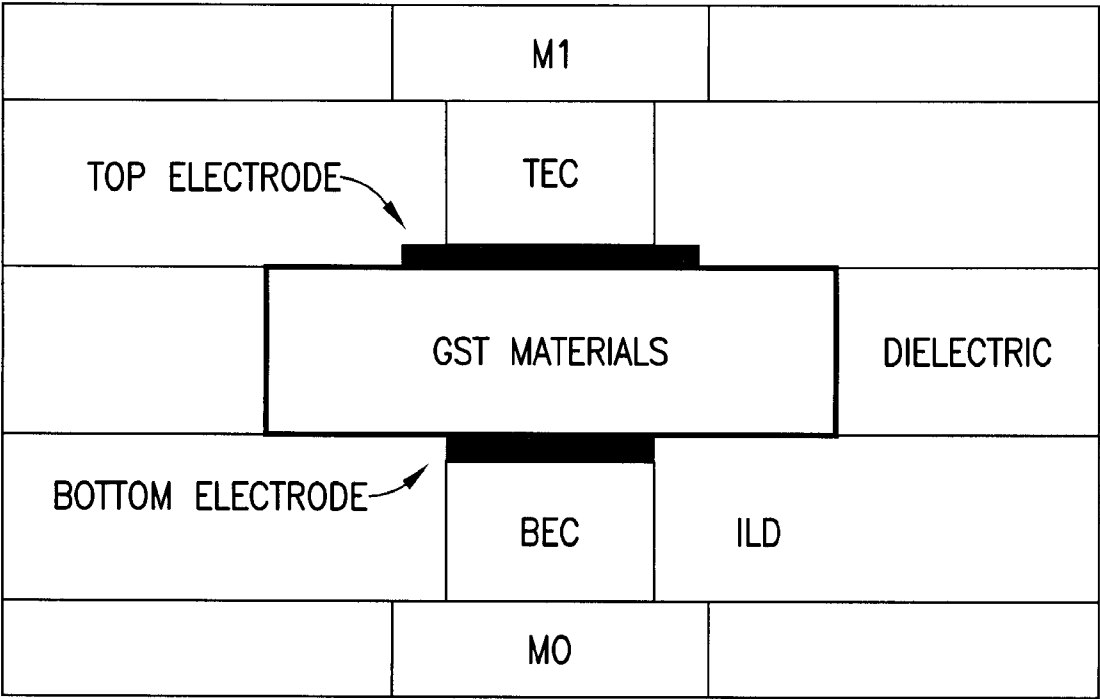


FIG.1

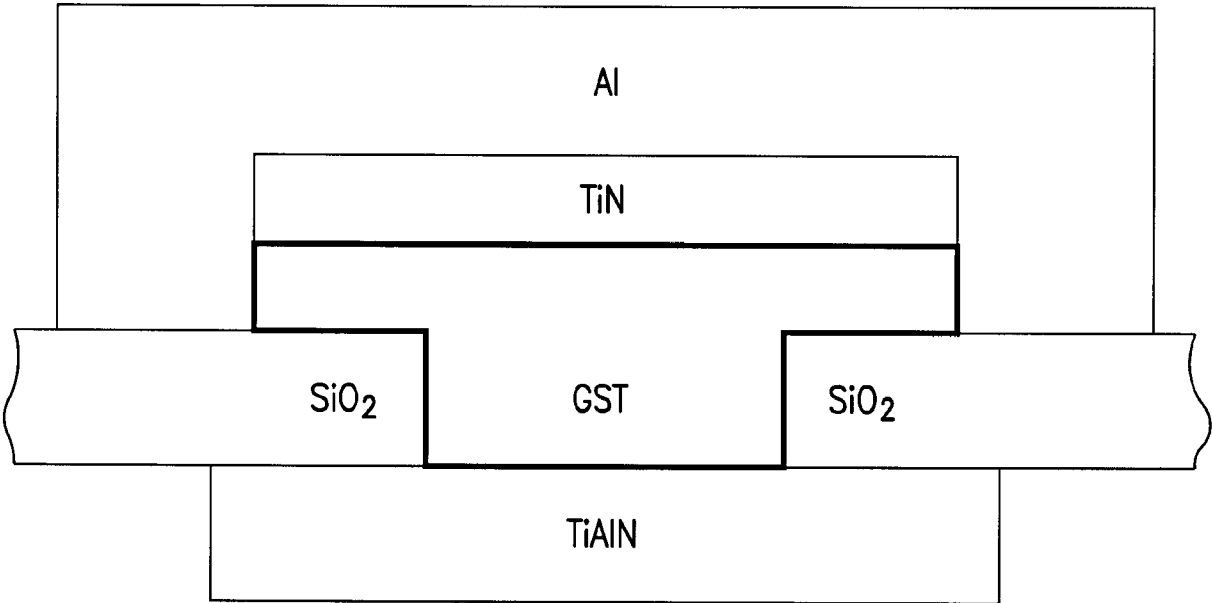


FIG.2

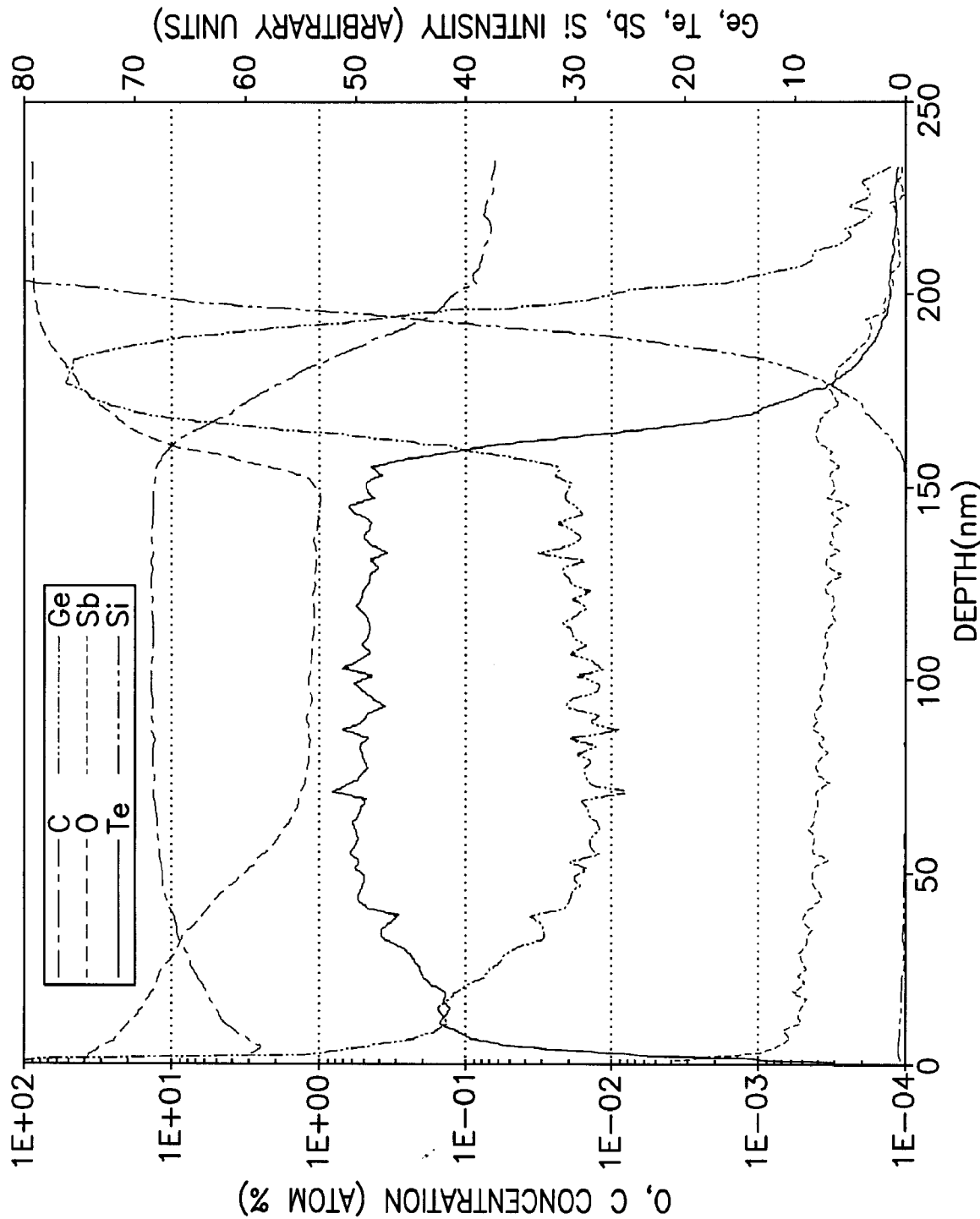


FIG.3

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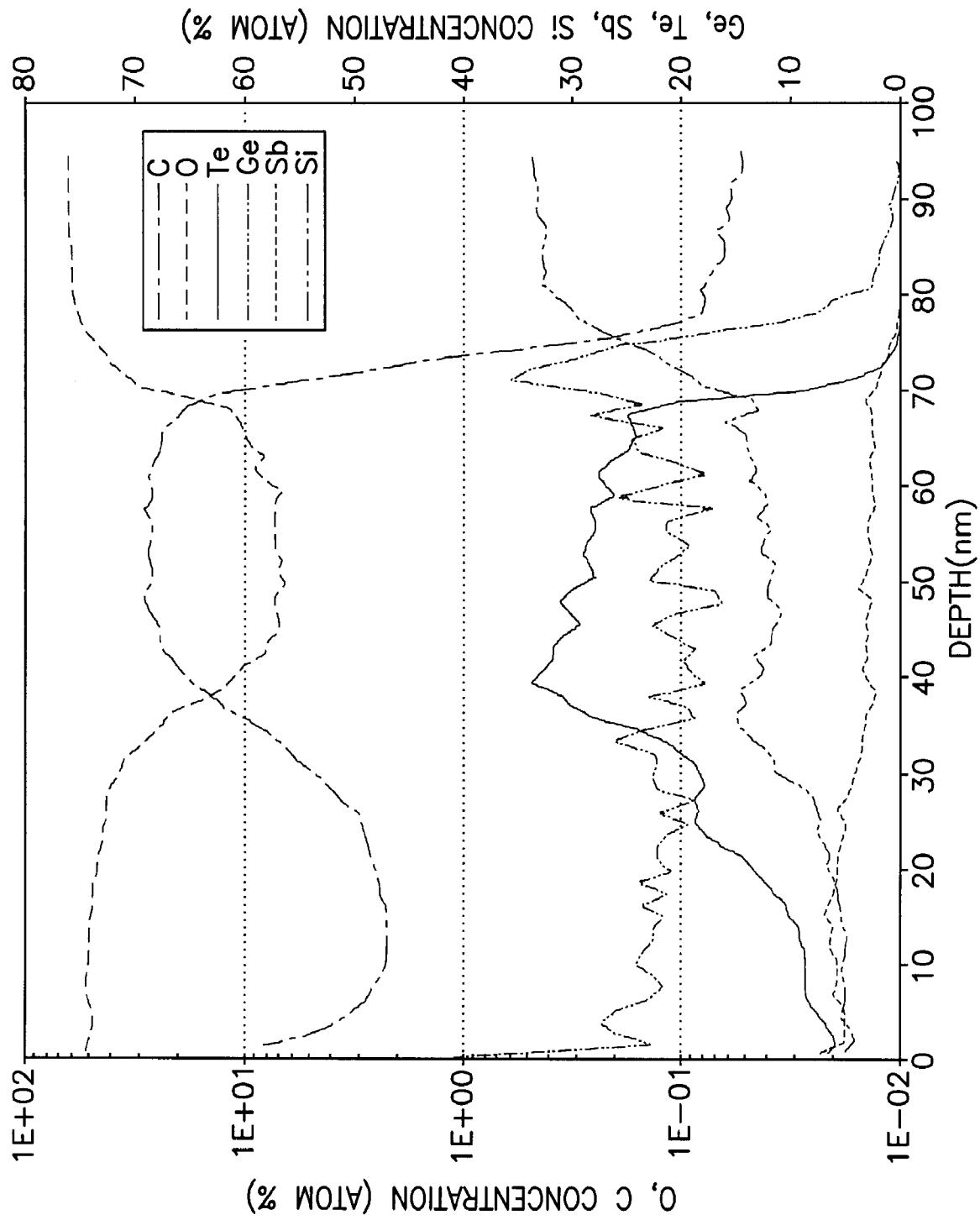


FIG.4

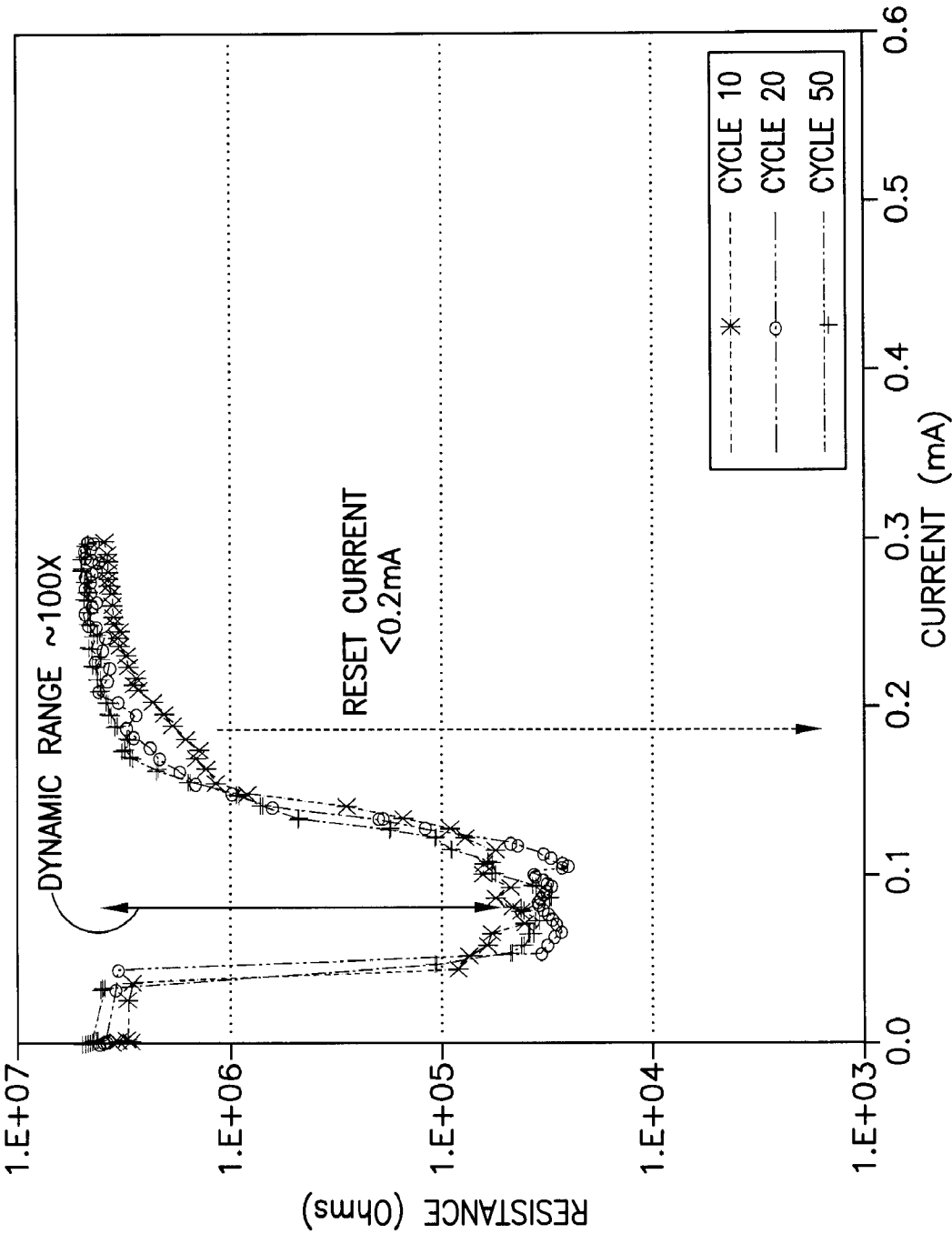


FIG.5

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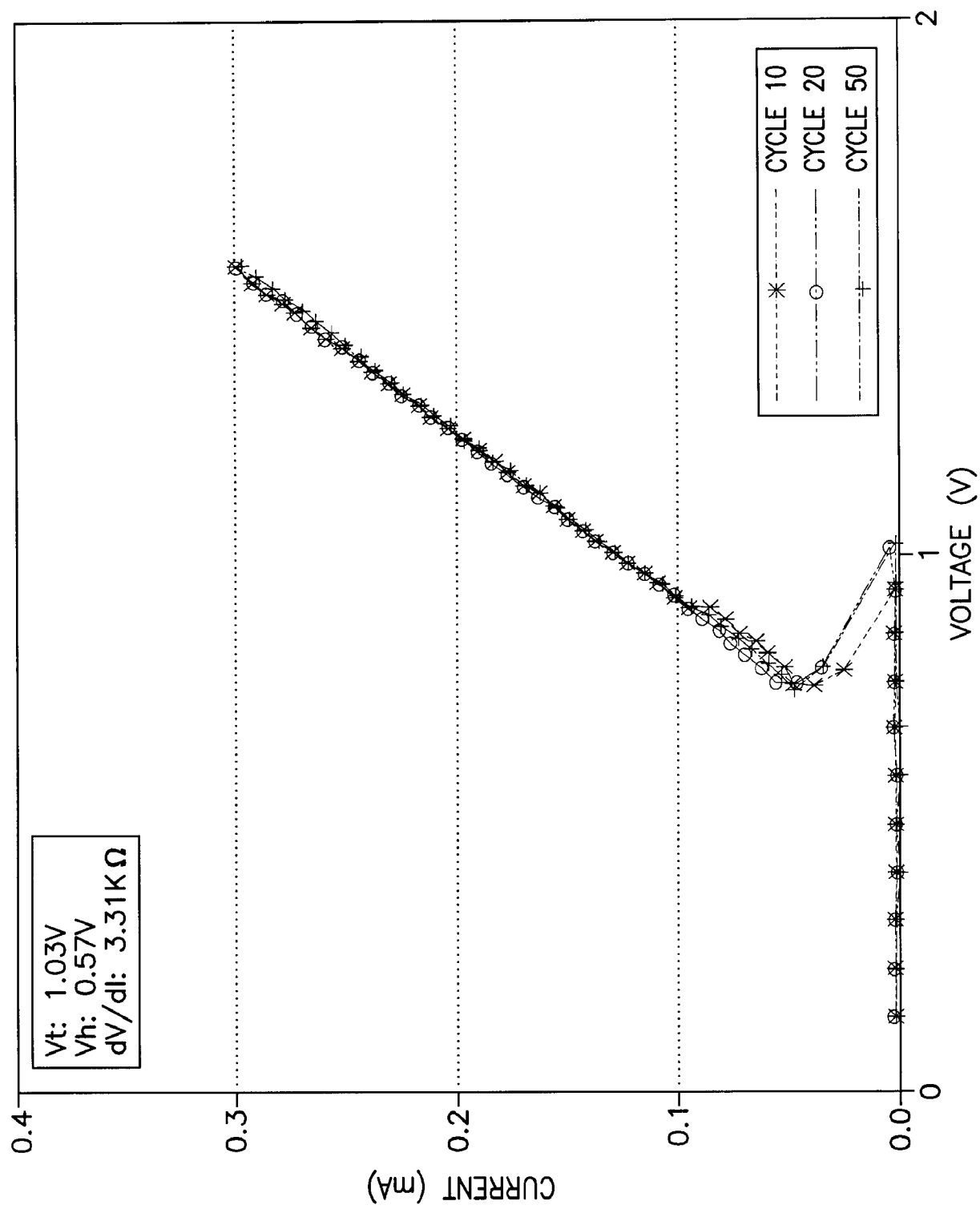
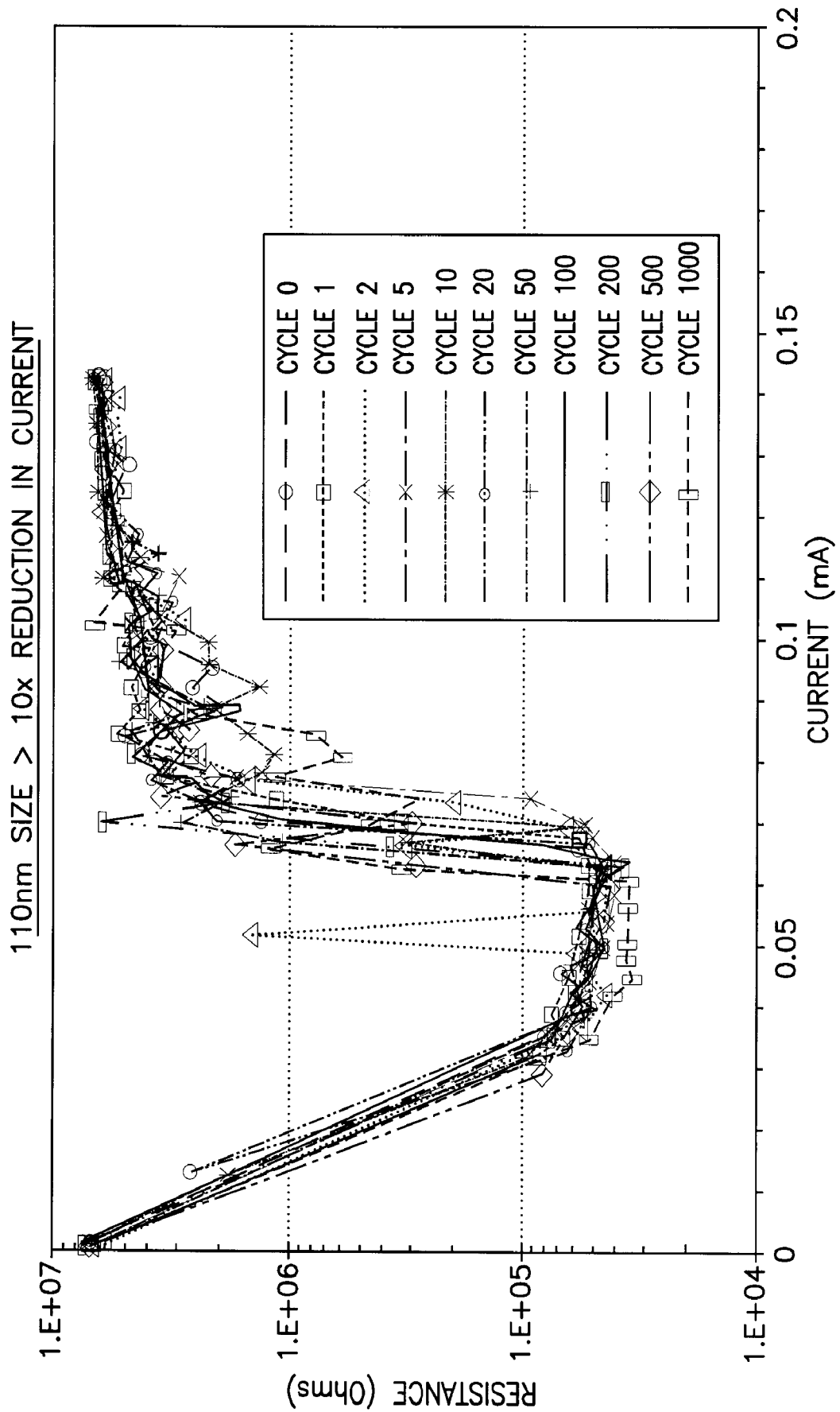


FIG.6

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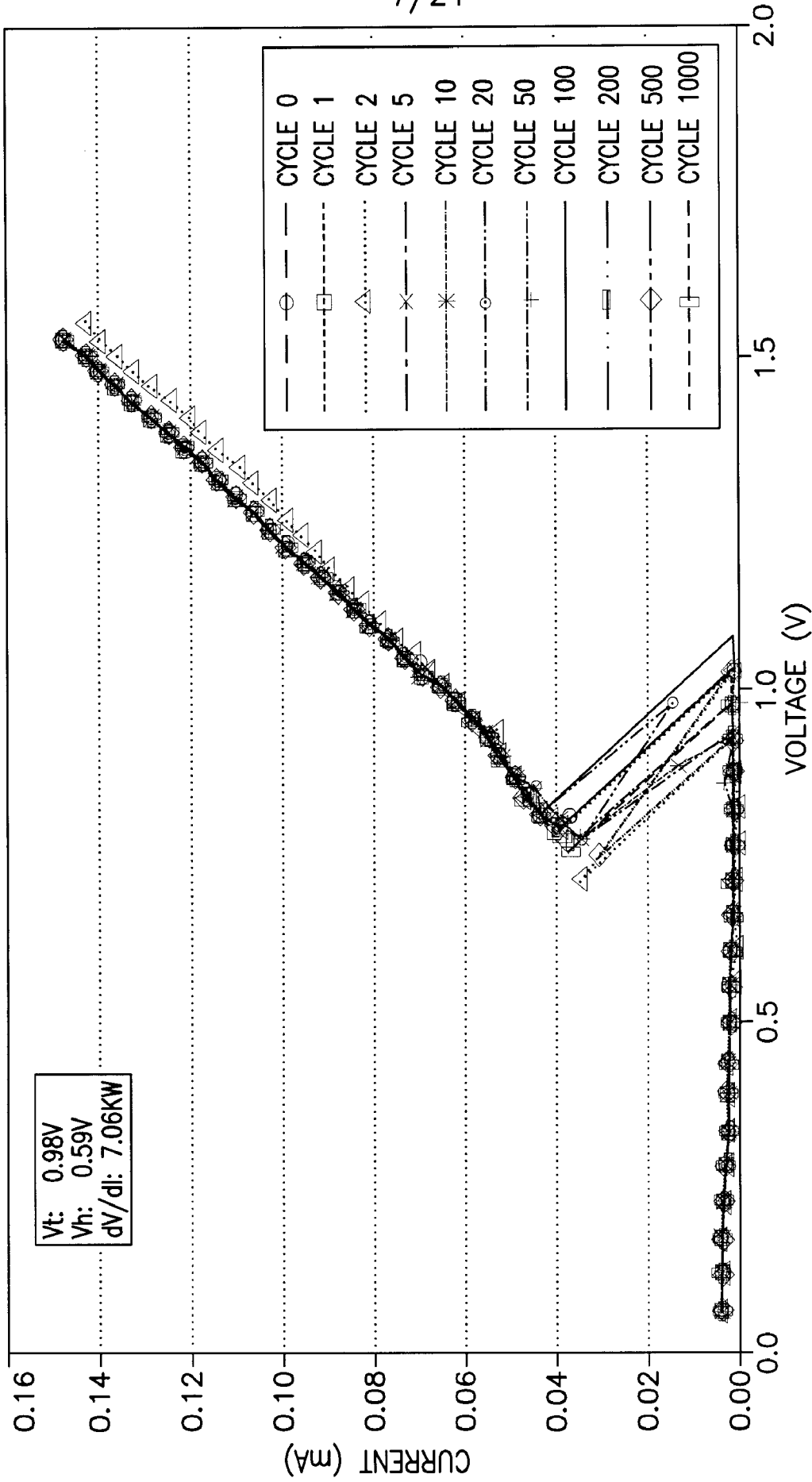


FIG.8

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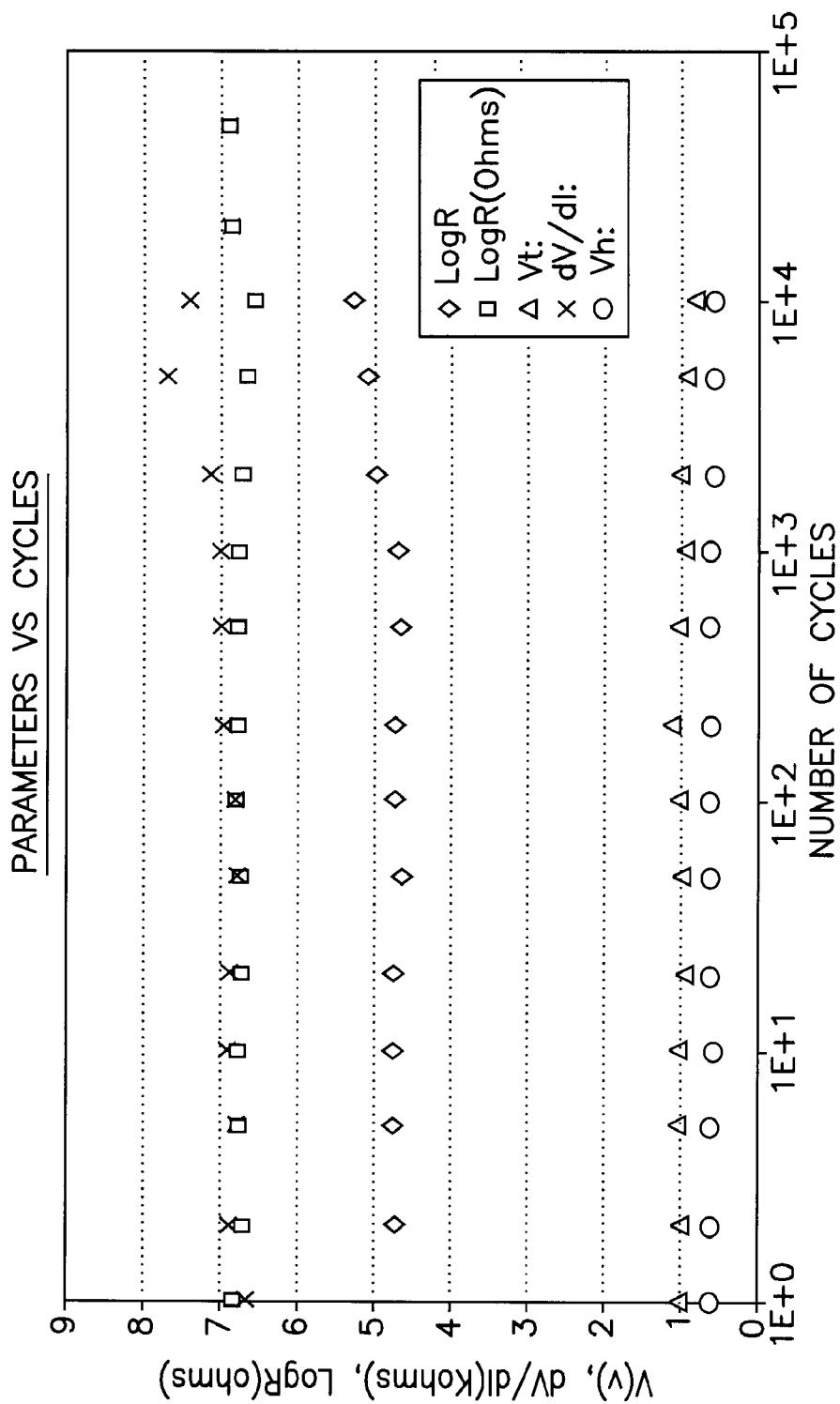


FIG.9

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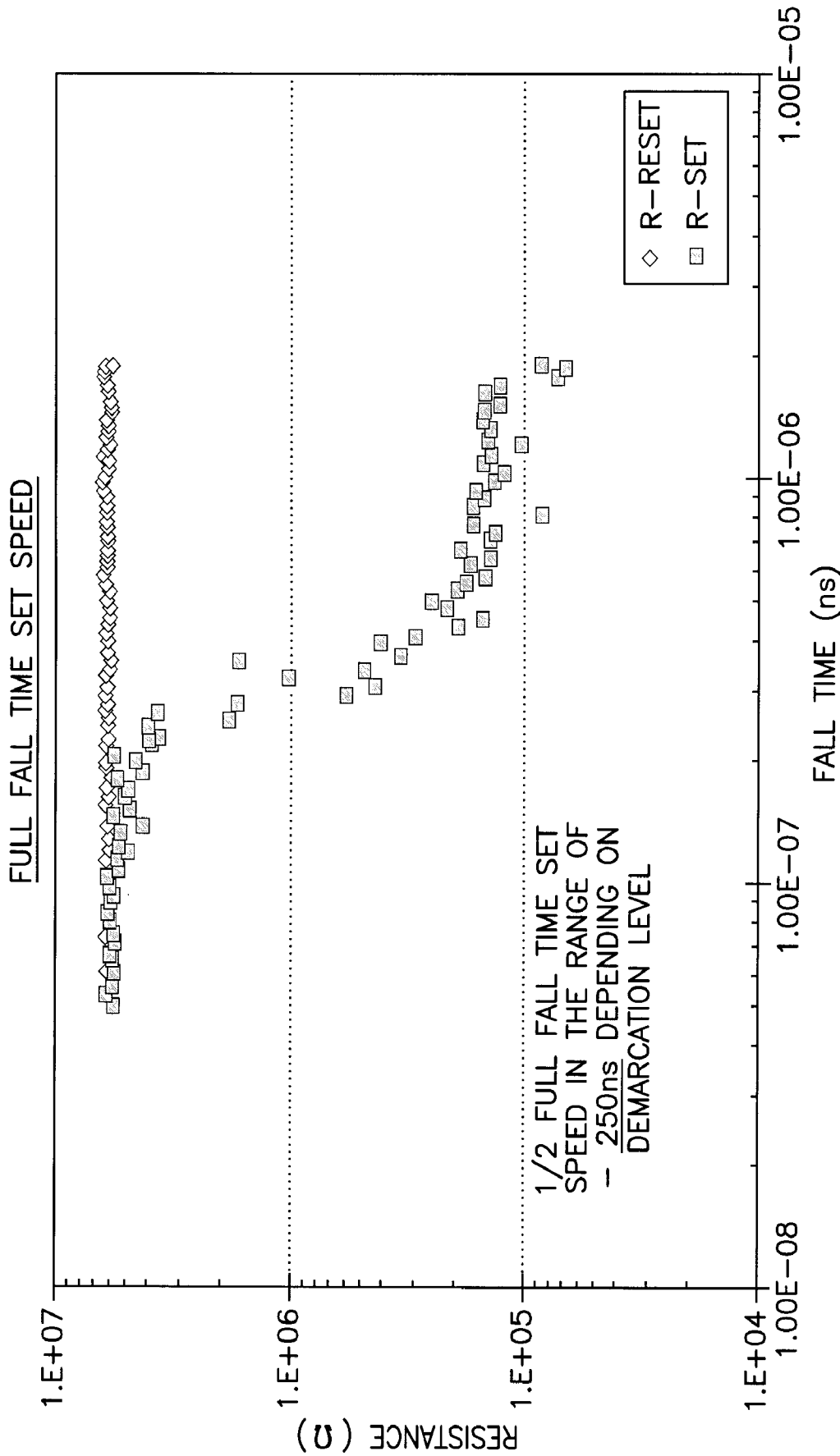
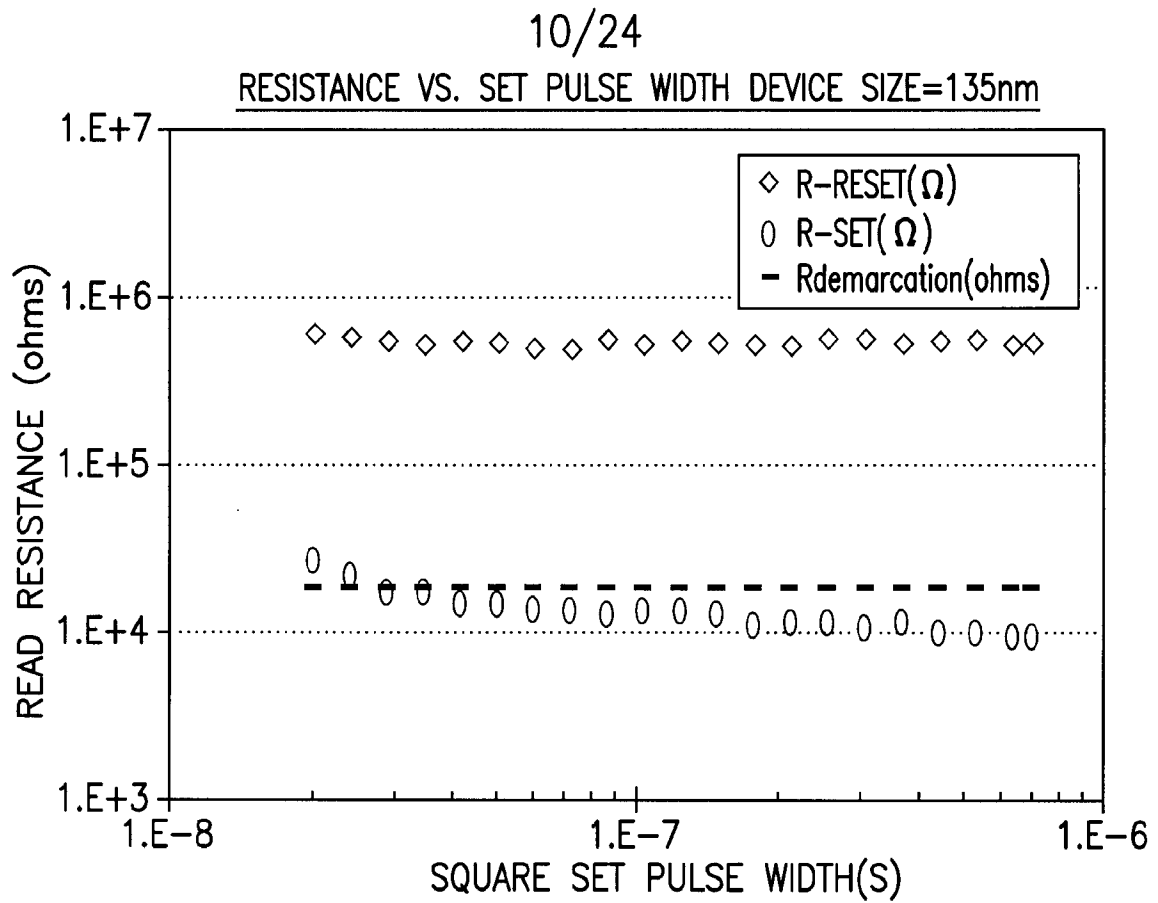
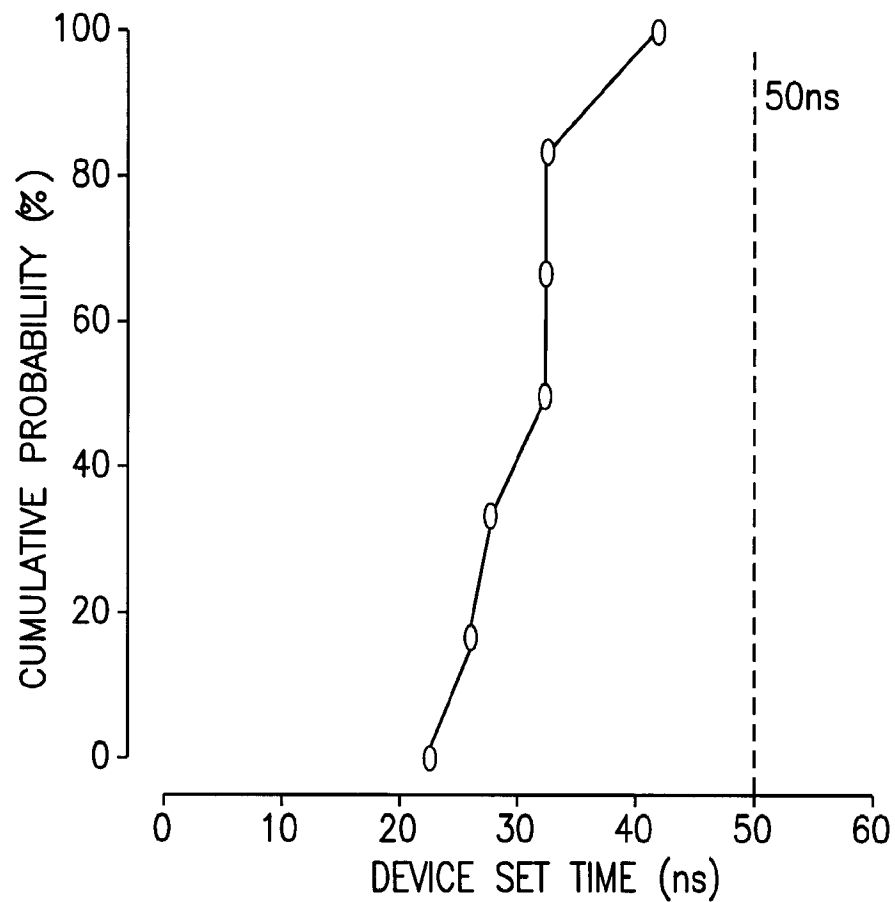


FIG. 10

**FIG. 11****FIG. 12**

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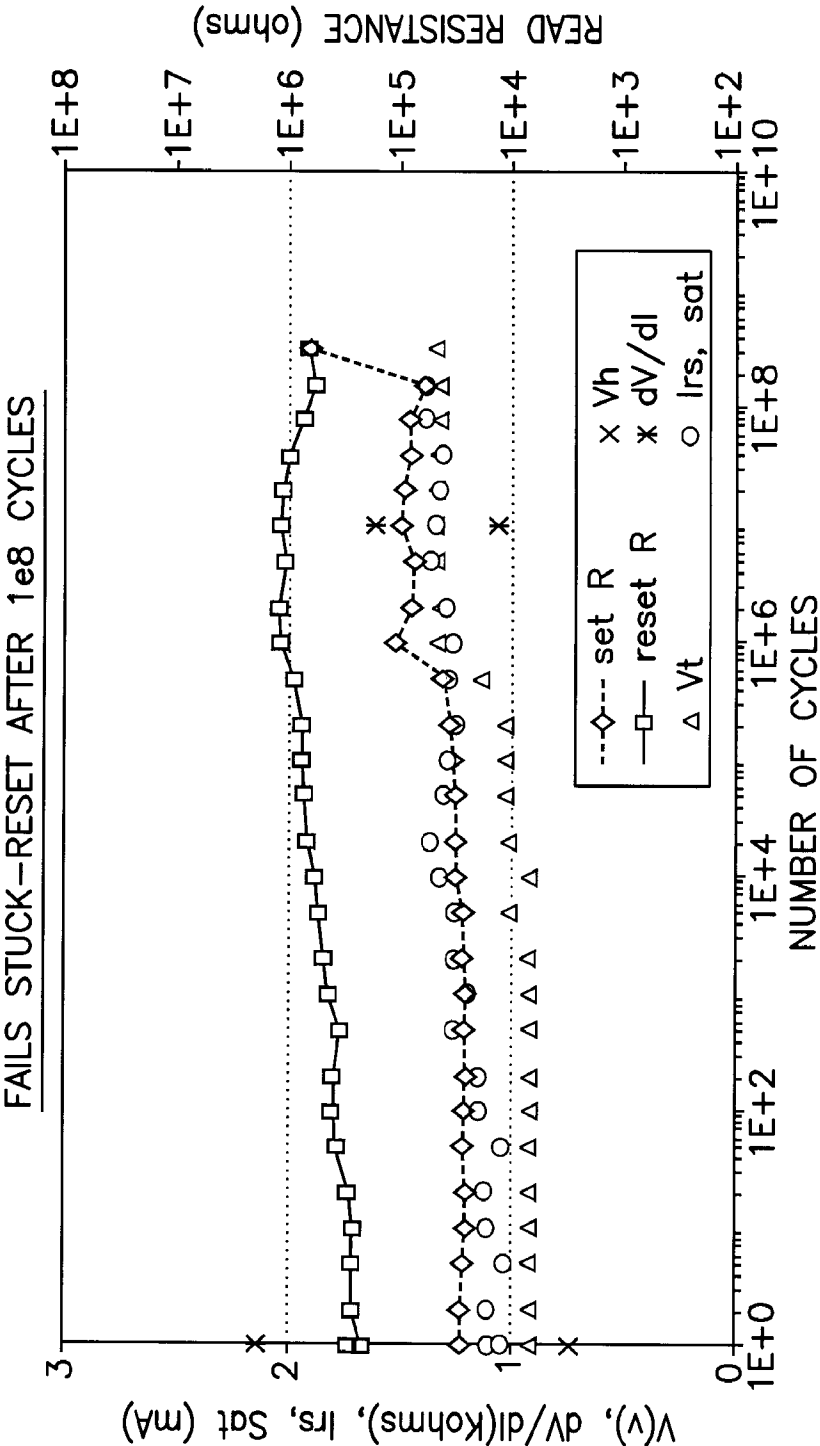


FIG.13

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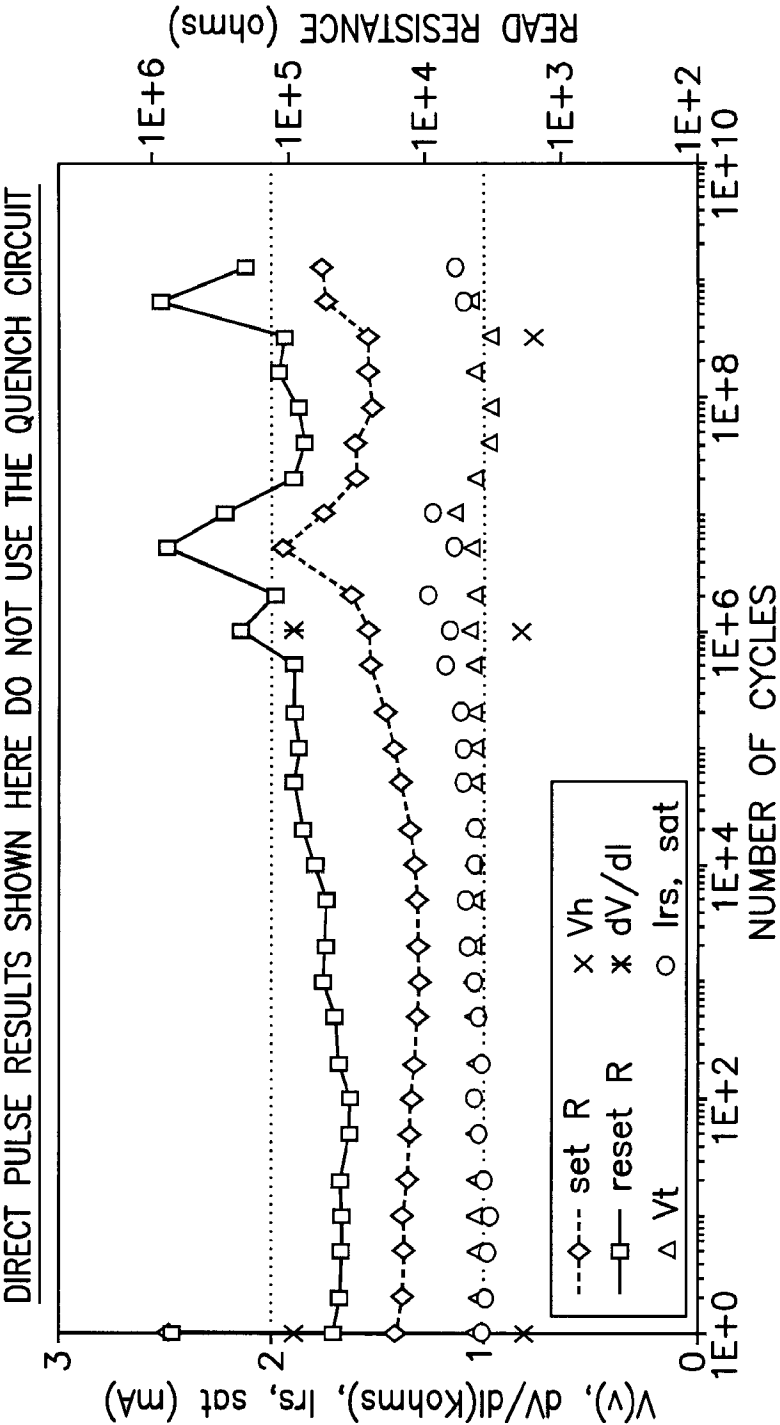


FIG.14

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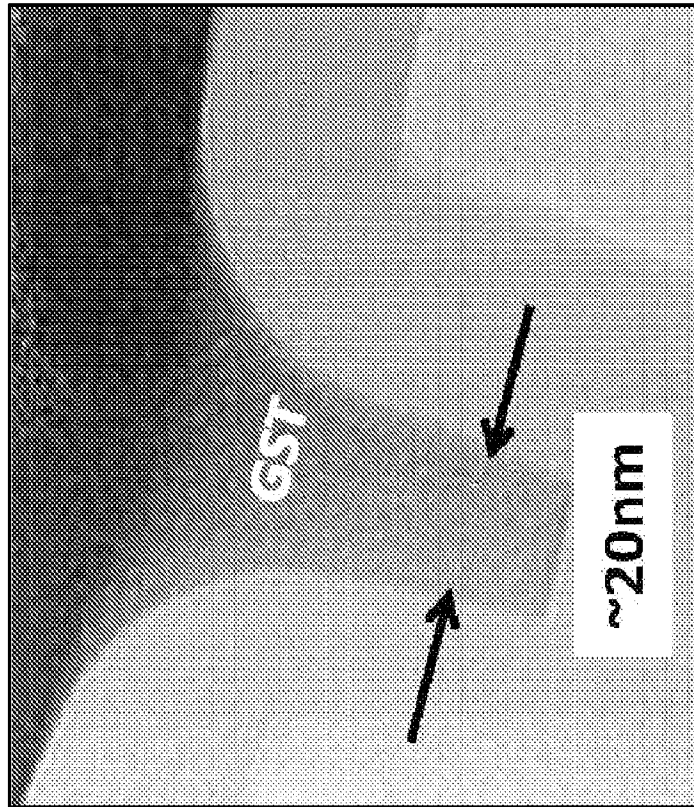


FIG.15B

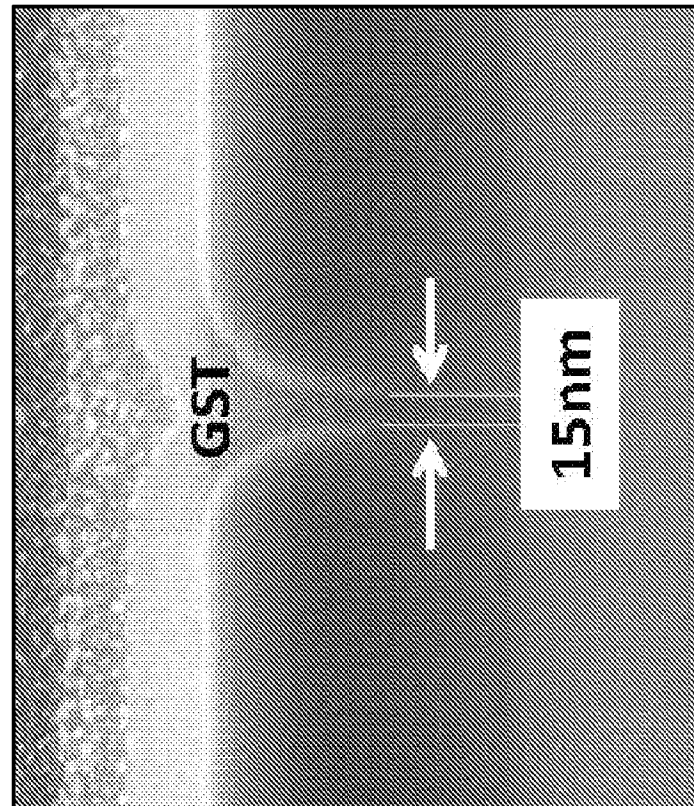


FIG.15A

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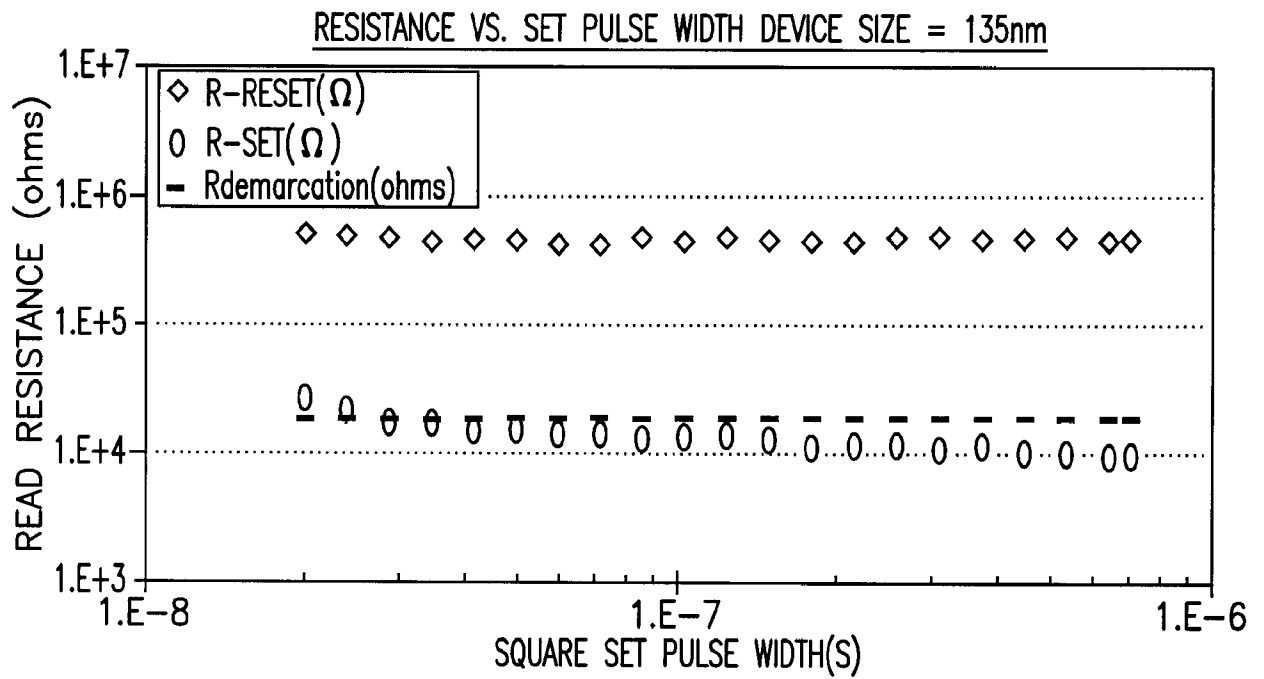


FIG.16A

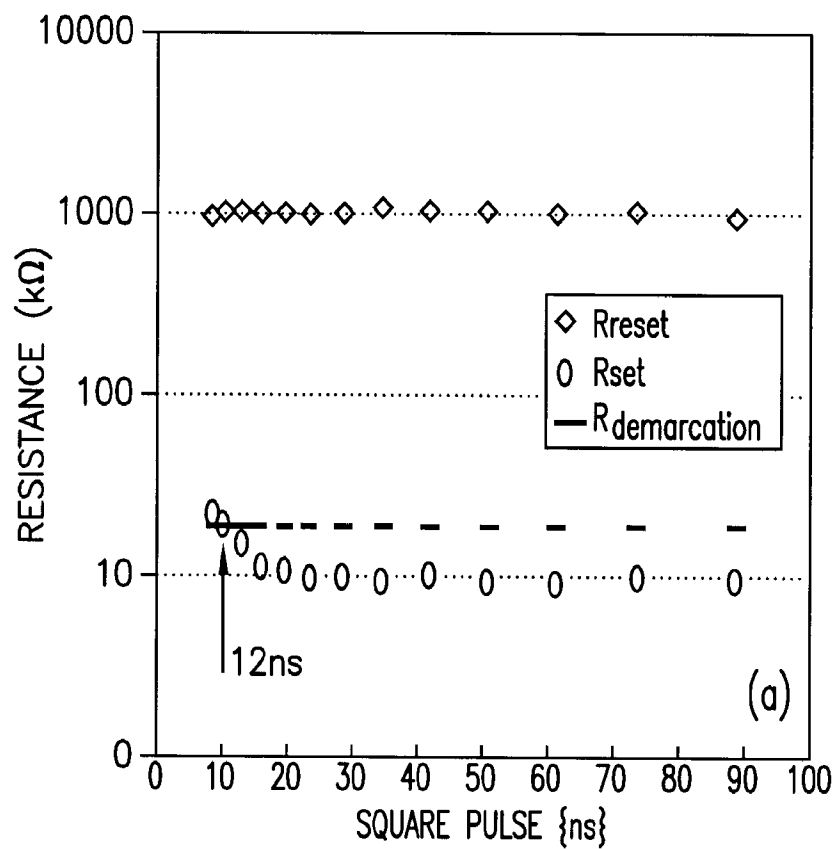


FIG.16B

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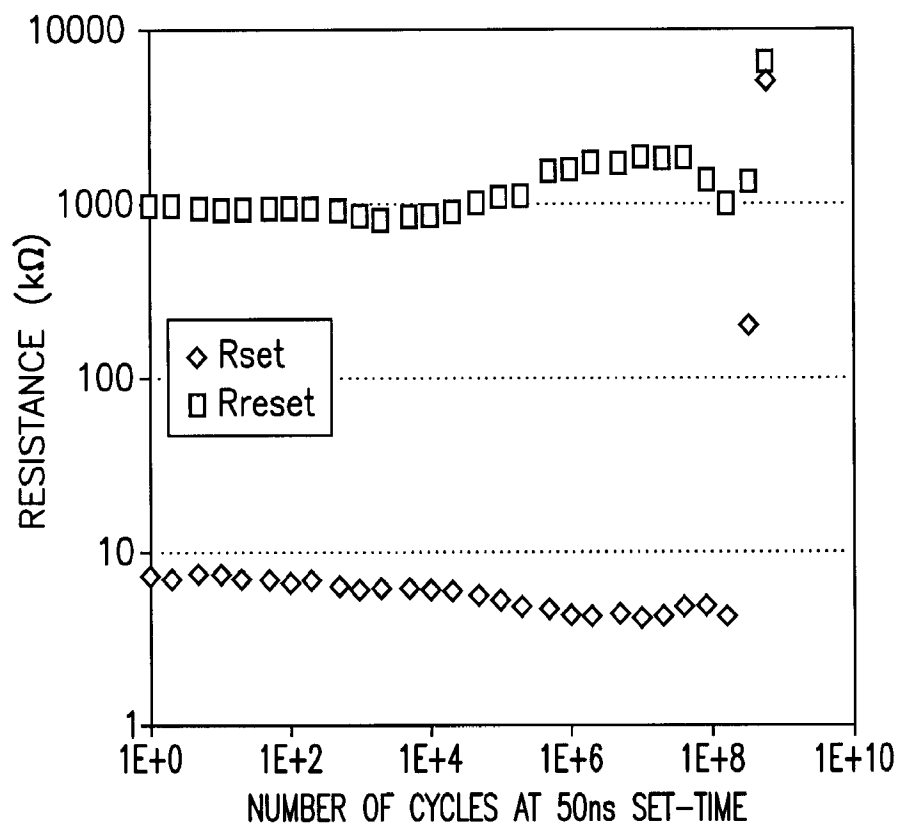


FIG.16C

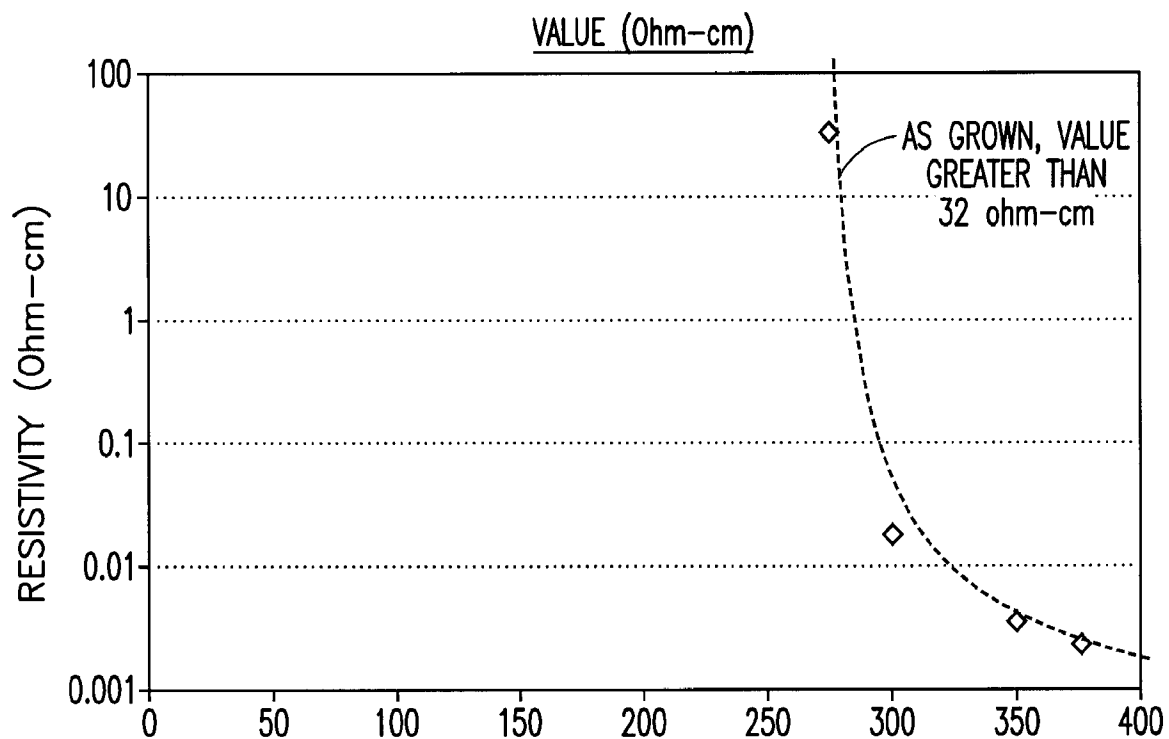


FIG.17

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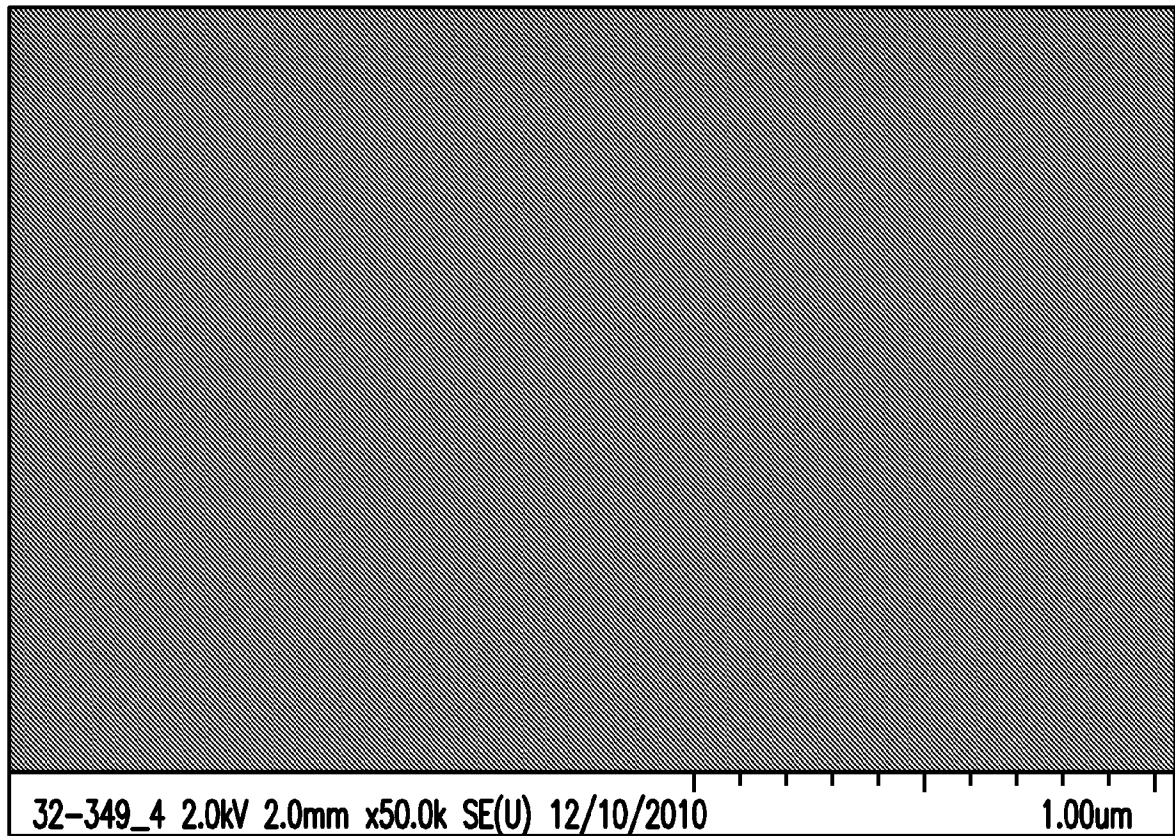


FIG.18

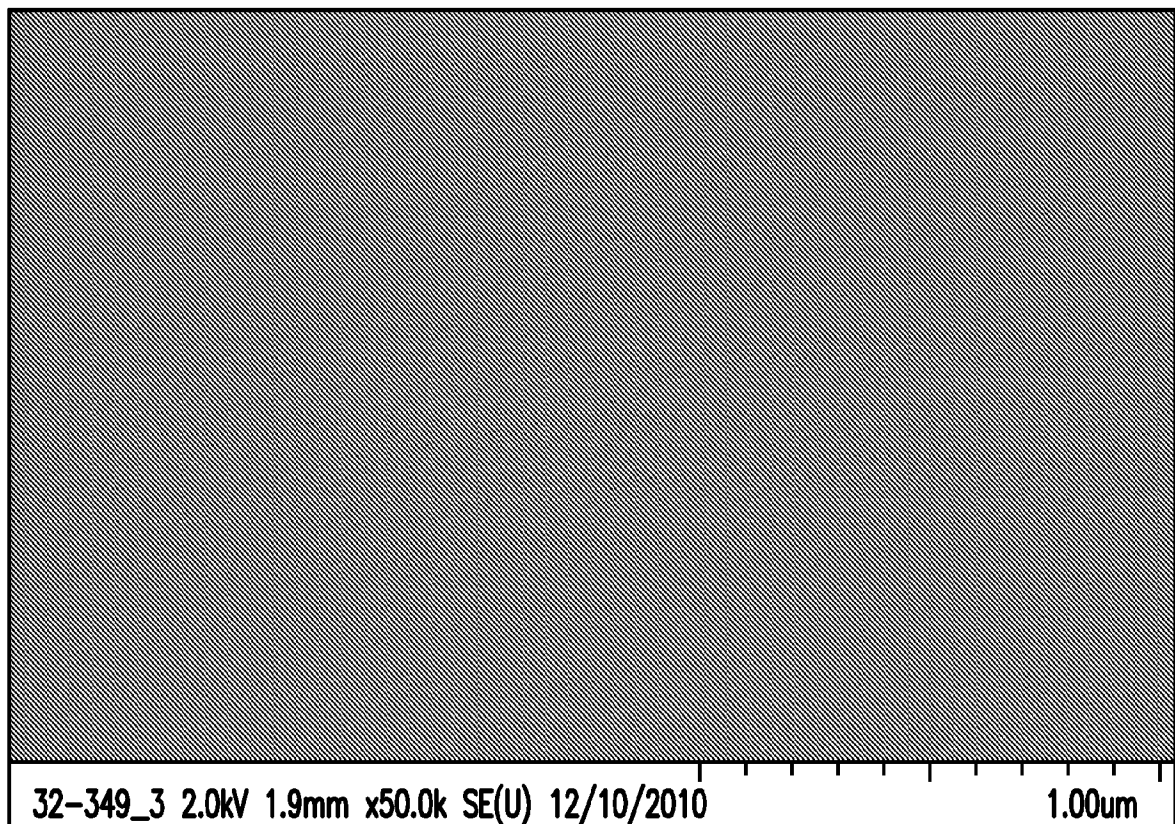
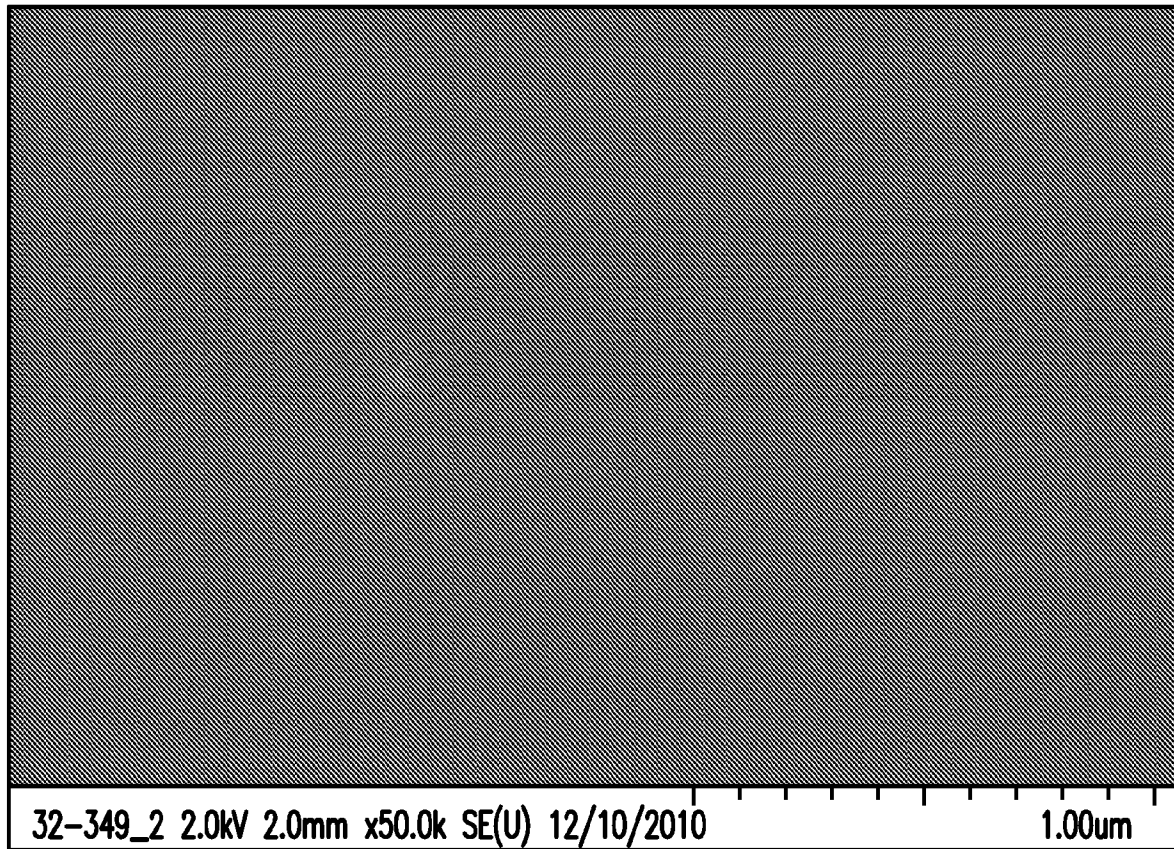
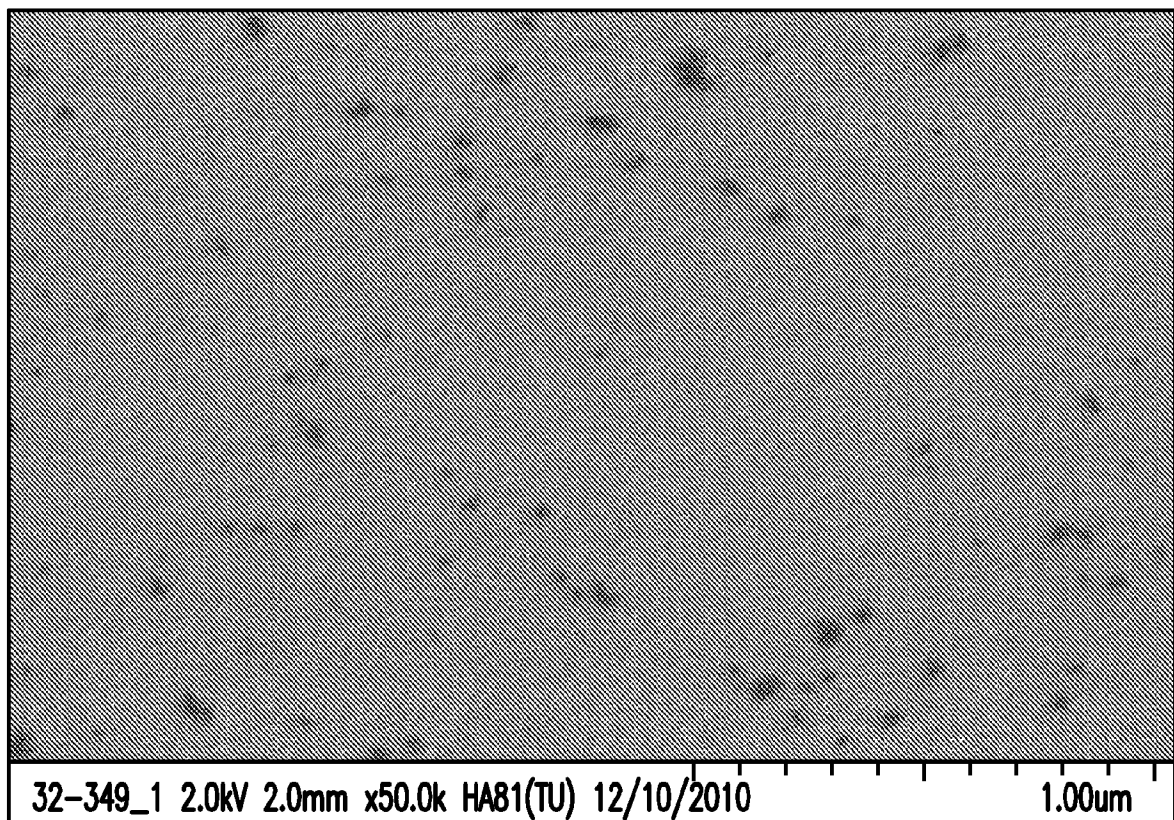


FIG.19

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**FIG.20****FIG.21**

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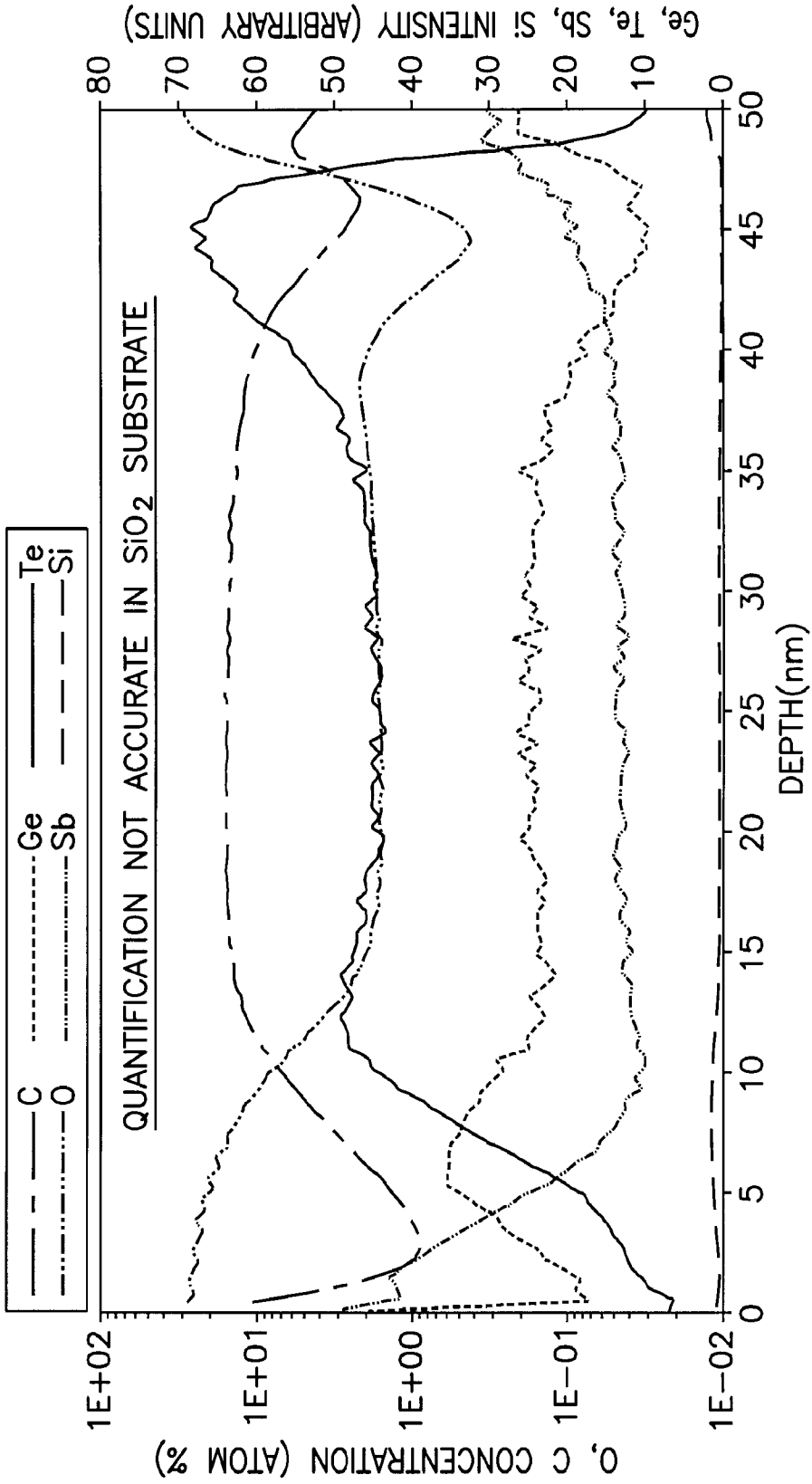


FIG.22

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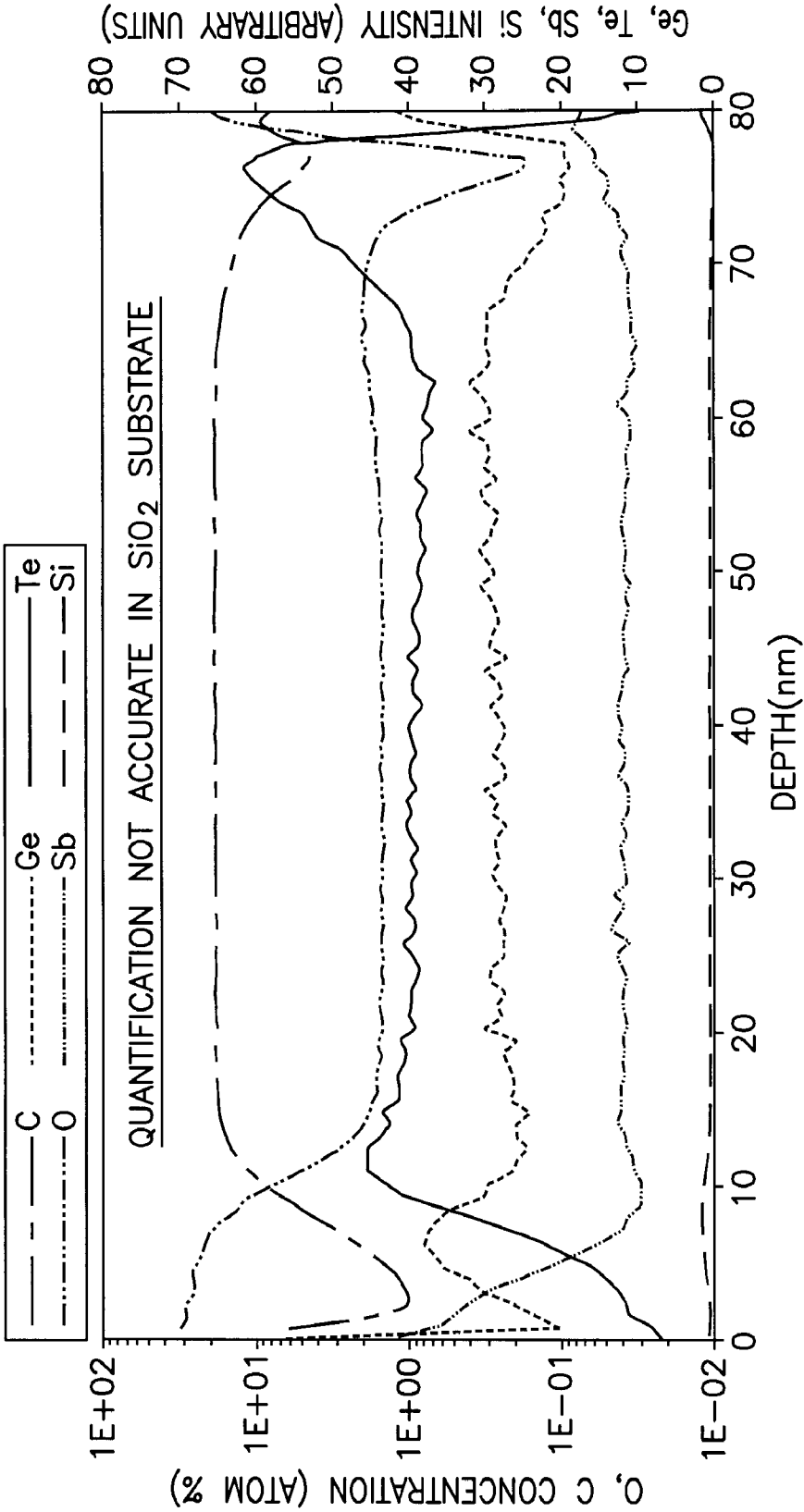


FIG.23

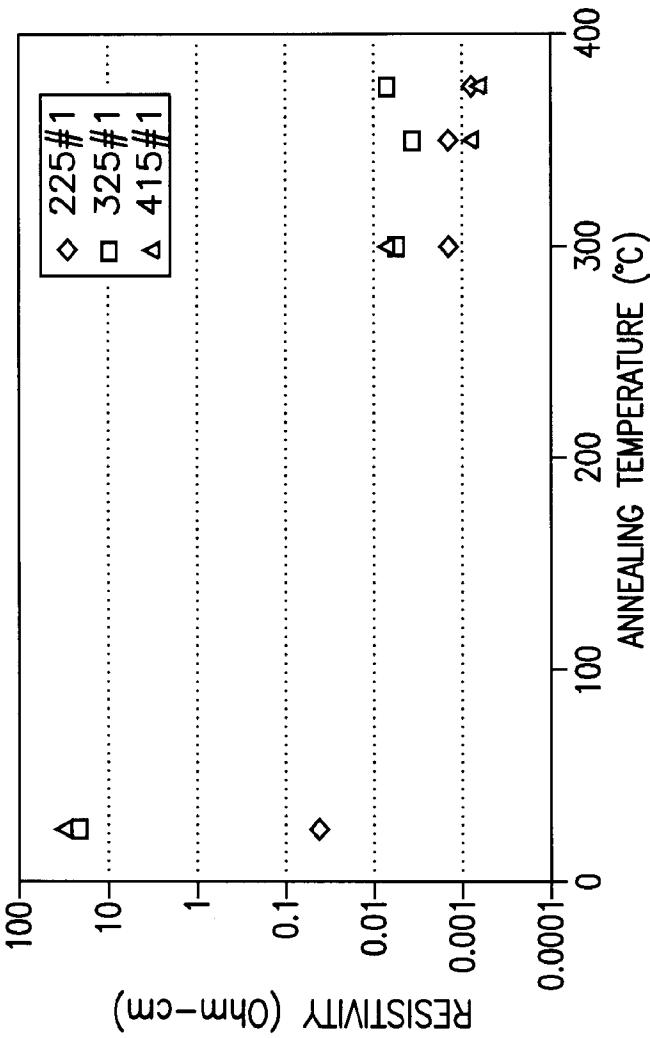


FIG.24

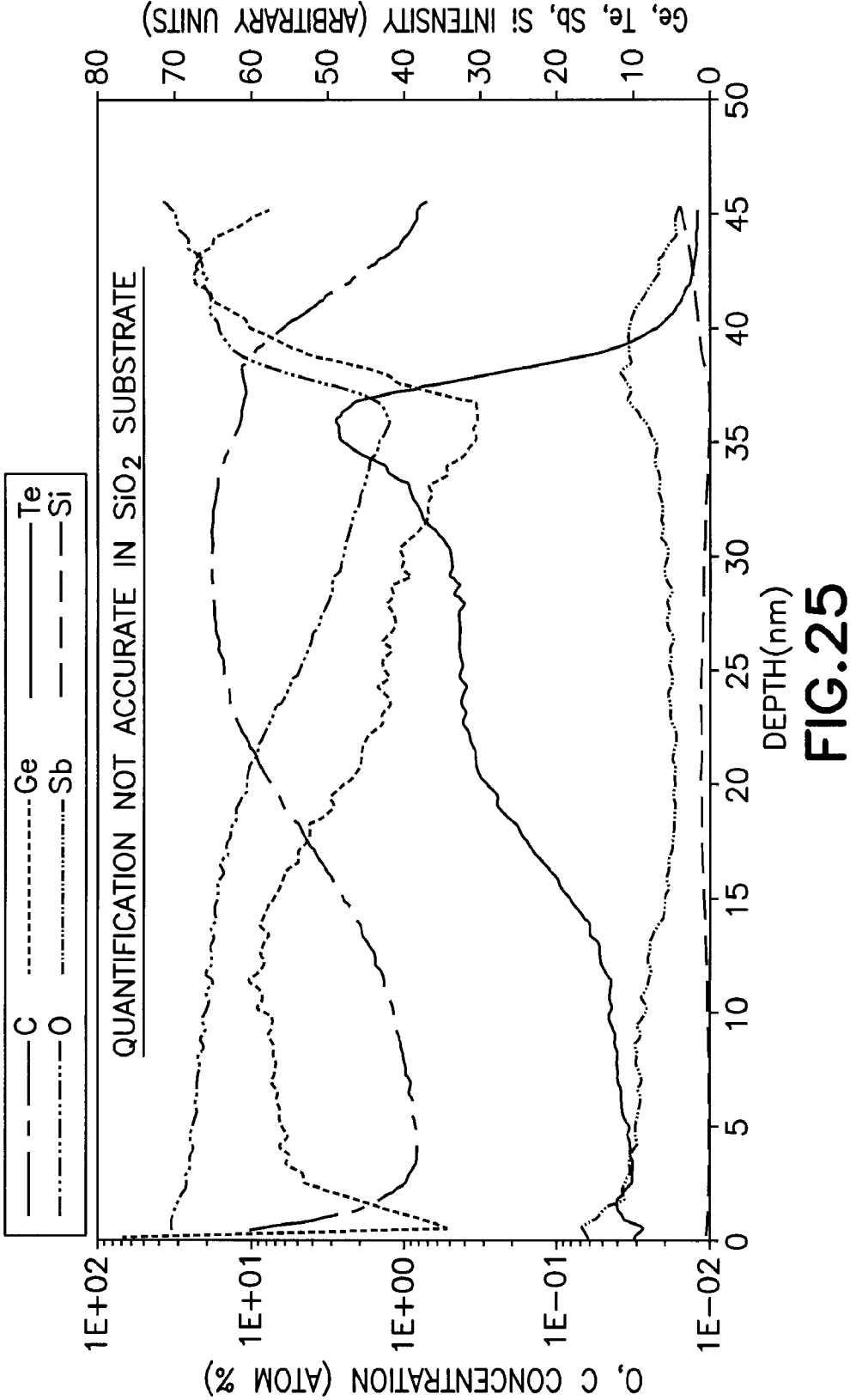


FIG.25

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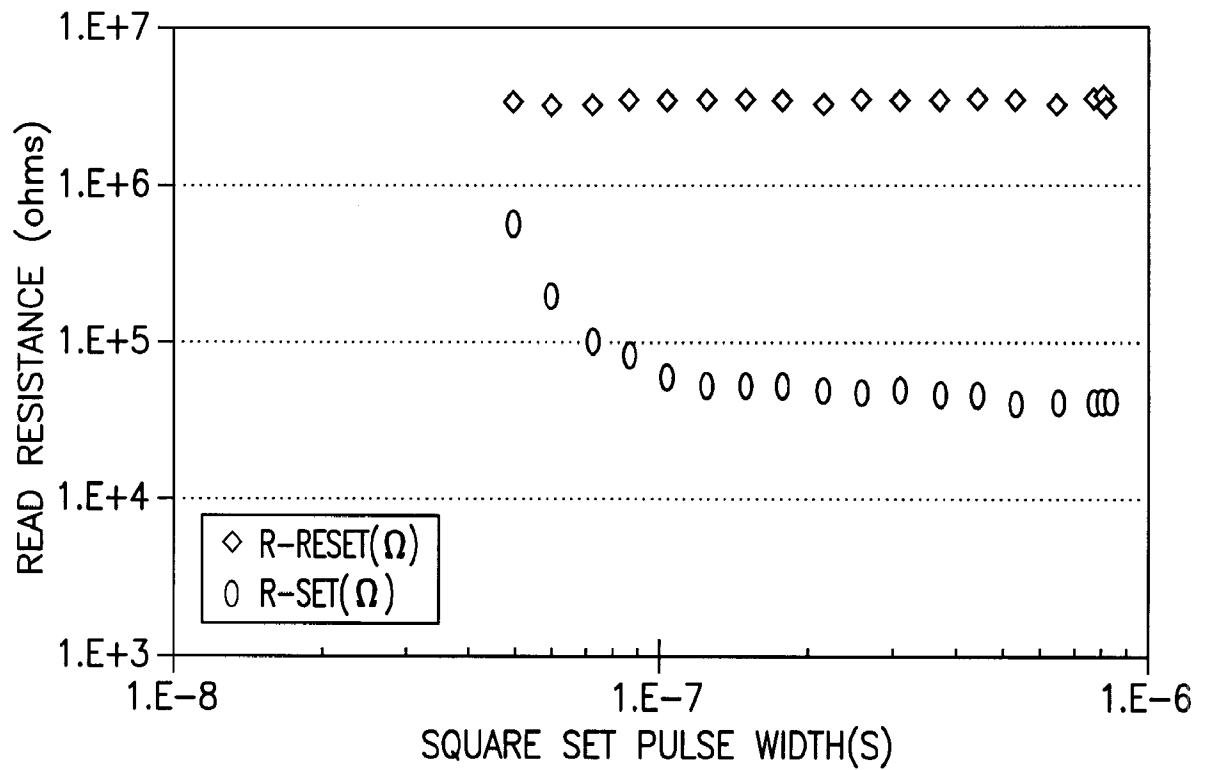


FIG.26

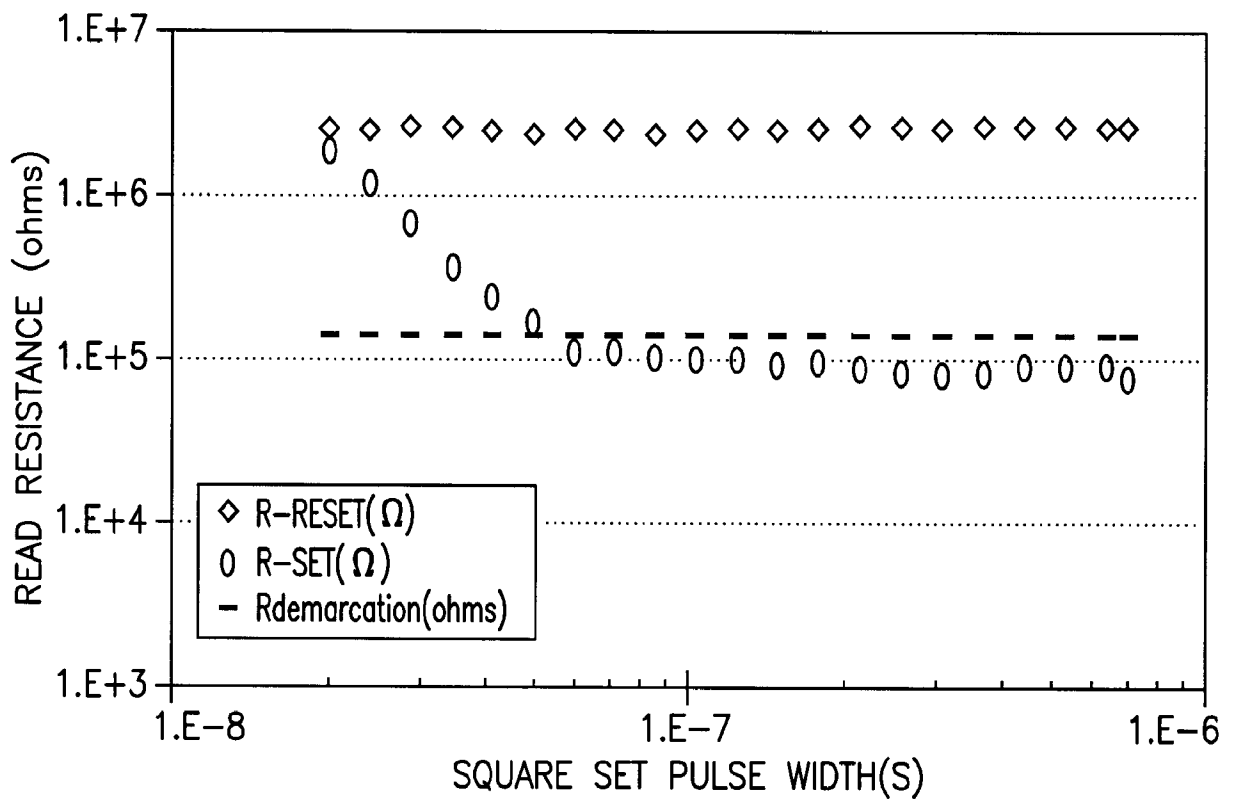


FIG.27

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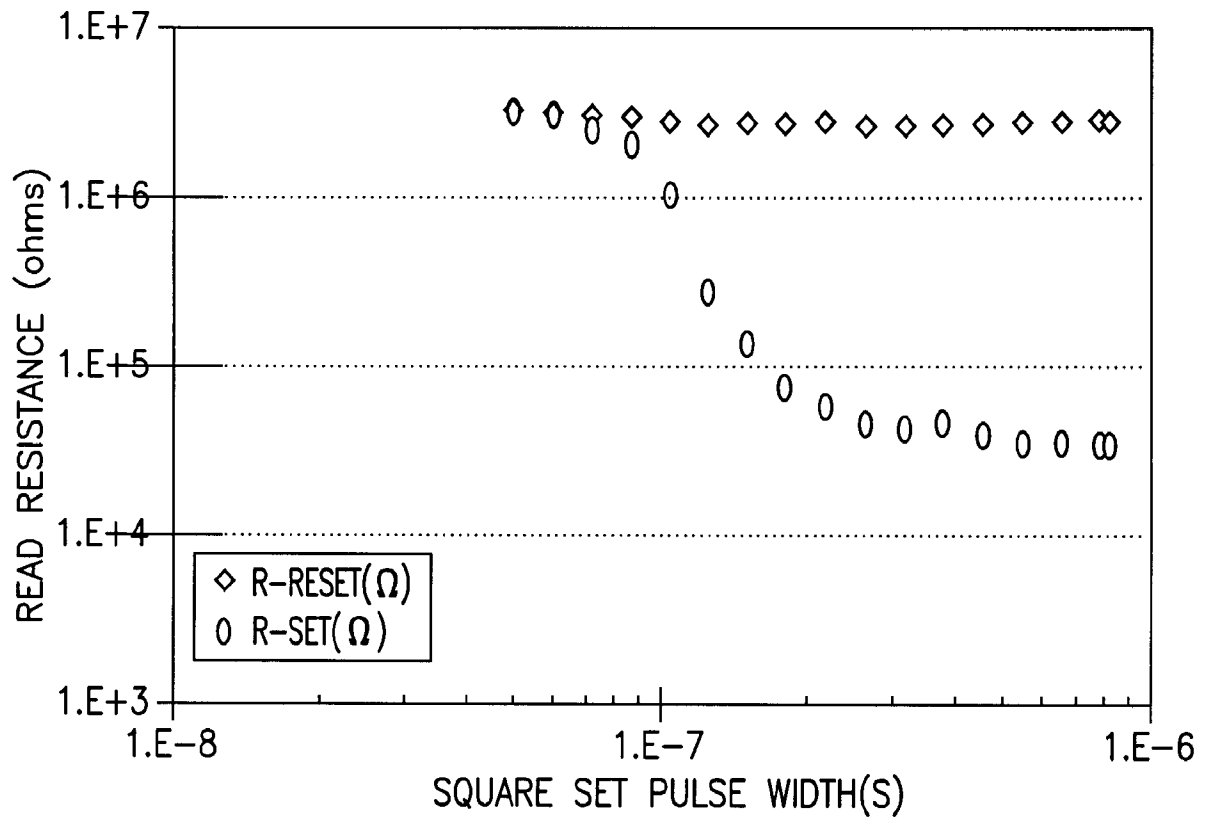


FIG.28

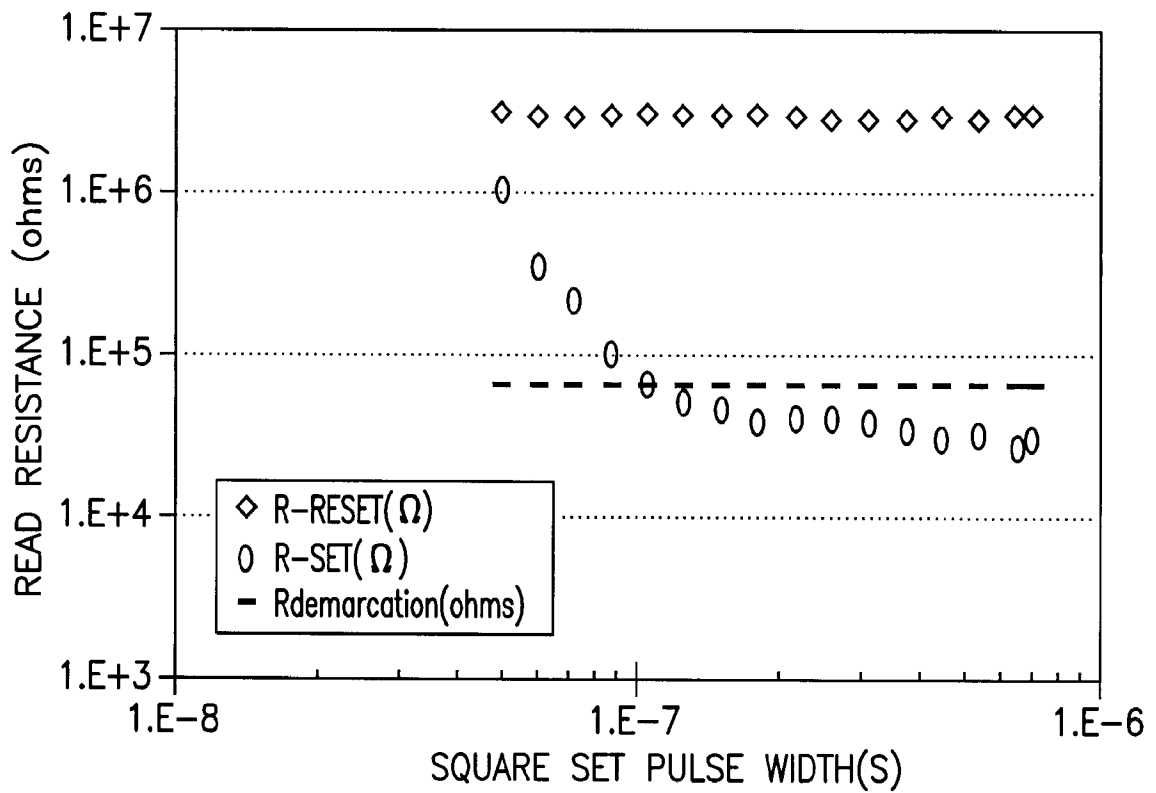


FIG.29

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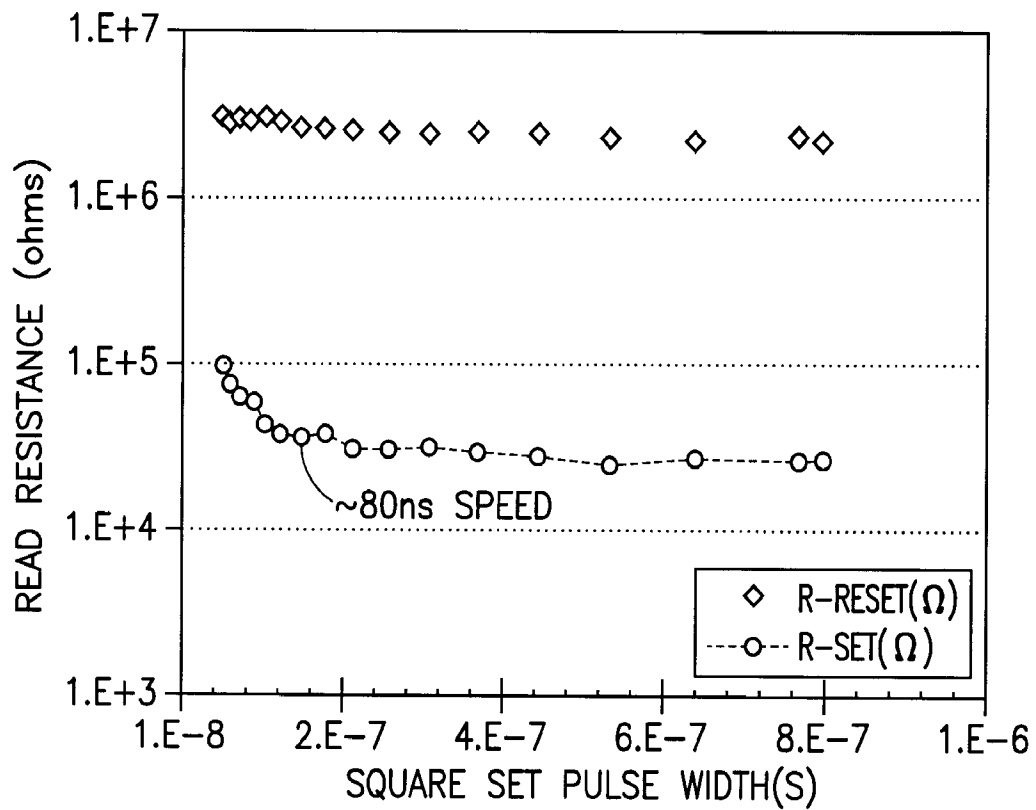


FIG.30

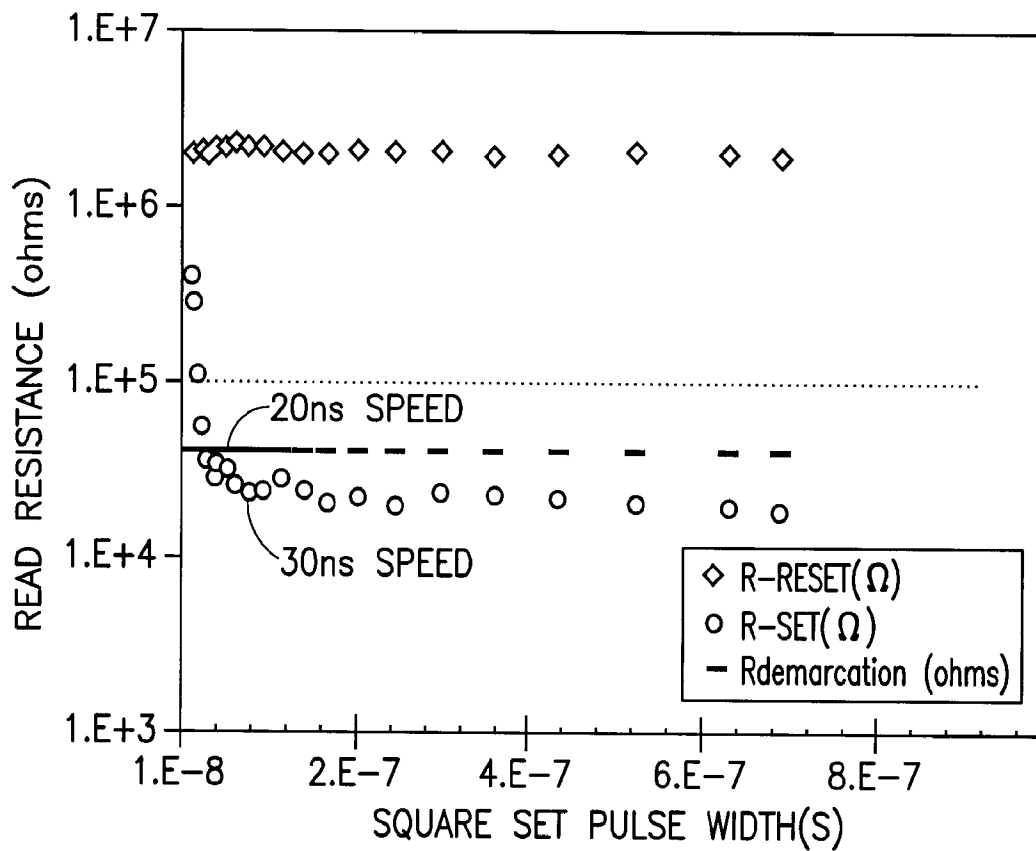


FIG.31