Electronic mechanism for resistance drift in phase-change memory materials: link to persistent photoconductivity

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Abstract

'Phase-change' memory materials, such as the canonical composition $Ge_2Sb_2Te_5$, are being actively researched for non-volatile resistive random-access memory applications. In these devices, ultra-rapid reversible transformations between metastable highly electrically conducting (degenerate-semiconducting) crystalline and more electrically resistive (semiconducting) glassy phases are produced by the application of appropriate voltage pulses. Multilevel programming, wherein more than two metastable resistance states can be stored in the memory material as different proportions of partially glassy/crystalline regions, allows more than one bit to be stored per memory cell. However, this route to increasing data density, without recourse to device-size down-scaling, is threatened by the phenomenon of 'resistance drift', wherein the electrical resistance of the glassy phase slowly increases with time, following a weak power-law dependence, after being written with a voltage pulse. In this paper, we propose an intrinsic electronic mechanism for the resistance drift by identifying it with the phenomenon of persistent photoconductivity that is commonly observed in a wide range of disordered semiconductors. We develop a model for it in terms of the long-time, deep-trap release and subsequent recombination of charge carriers, akin to that which is believed to be responsible for the long-time photocurrent decay in amorphous semiconductors, such as hydrogenated amorphous silicon. In this case, the parameters controlling the resistance drift are the widths of the (localized) valence- and conduction-band tails in the vicinity of the bandgap. Hence, there is the potential for mitigating resistance drift in the amorphous state of phase-change memory materials by suitable material engineering (e.g. via compositional or fabricational control) to control the extent of band-tailing, thereby facilitating the future introduction of multistate memory.

1. Introduction

Phase-change random-access memory (PCRAM), a form of electronic non-volatile resistive random-access memory (RRAM) technology, is based on Joule-heating. A voltage-pulse-induced, reversible and ultra-fast ('SET') transformation to an electrically-conductive (degenerate-semiconductor/near-metallic) crystalline (*c*-)state (logic state '1'), takes place on heating an electrically-resistive (semiconducting) glassy (*g*-)phase (logic state '0'); the reverse, even faster ('RESET') transition back to the melt-quenched *g*-state occurs via an intermediate liquid state on heating the *c*-phase. In this way, binary bits of information {0,1} are encoded as metastable structural states of the material [1-3]. Materials exhibiting such ultra-fast transitions (durations of order a few nanoseconds), and which also have a significant electrical resistivity contrast between *g*- and *c*-phases (of 2-3 orders of magnitude), include alloys such as the canonical composition, $Ge_2Sb_2Te_5$ (GST), along the GeTe – Sb_2Te_3 compositional tie-line [4].

PCRAM technology [5], based on materials such as GST, is extremely promising and has now started to be commercialized as a replacement for Si-CMOS flash-memory. An example is the 3D-XPoint™ technology, jointly developed by Intel and Micron and announced in 2015, forming the basis of their respective products, with brand names Optane and QuantX, and launched in 2017. However, there are still a number of challenges if PCRAM is eventually to be used as a 'universal memory' – i.e. a high-density, non-volatile memory having dynamic random-access memory (DRAM)-like switching times (~1ns) [1]. These challenges include: i) decreasing the rate-limiting SET (crystallization) switching time down to the ~1ns timescale needed for DRAM replacement by non-volatile PCRAM, while still retaining sufficiently long-time stability of the glassy logic state {0} [6]; ii) increasing the write-erase cycling durability to the value of ~10^{16} cycles needed for DRAM operation; and iii) ideally, increasing the data-storage density, e.g. by device down-size scaling. Such PCRAM materials with sufficiently large electrical contrasts between *g*- and *c*-phases can also be used, in principle, to store multiple bits per memory cell, wherein different proportions of partially *g*-/*c*-states can be programmed; up to 16 (= 2^4) distinct resistivity levels (i.e. corresponding to 4 bits/cell) have been demonstrated [7]. However, effectively, a *continuous* range of programmable resistance levels can be written in PCRAM cells, as continuously variable proportions of resistive *g*- and conducting *c*-phases, meaning that such devices can also function as 'artificial synapses' [8], with application in neuromorphic ('brain-like') computing [9].

However, the potential for multilevel memory operation is seriously compromised by a slow, time-dependent increase ('drift') of the electrical resistance exhibited by PC materials in the RESET *g*-state (but *not* in the SET *c*-state) [5, 10-27]. This resistance drift exhibits experimentally a weakly power-law time dependence under isothermal conditions, extending over at least 14 orders of magnitude in time, from times of ~30ns [13] up to at least 30 days (~$3x10^6$ s) [28]. The functional dependence of the resistance drift can be written as:

$$R(t) = R(t_0)\,(t/t_0)^{\upsilon}, \quad (1)$$

where the ‘drift’ exponent, υ, i.e. the slope of a log-log plot of resistance versus time, typically has the value υ ~ 0.1 [5, 6, 8-17]. There is some evidence that different PCRAM materials can exhibit slightly different drift exponents, e.g. υ ~ 0.13 for *g*-GeTe, whereas υ ~ 0.1 for *g*-GST [5]. Thus, resistance drift can cause differently initially programmed resistance levels, in multilevel memory operation, to cross with time, e.g. due to variations in drift exponents between cells (Figure 1b), thereby reducing the effective number of bits that can, in practice, be written in a memory cell [5]. Although drift-tolerant, modulation-coding techniques can mitigate this effect to a certain extent [28, 29], nevertheless it would be much more preferable if the drift effect itself could be controlled and reduced, and, ideally, eliminated. However, this latter approach is only really feasible once a full understanding of the origin of the resistance drift is available.

The physical origin of this resistance drift is still not understood. Several explanations for the origin of resistance drift have been proposed [5]. Two extrinsic mechanisms, based on the time evolution of amorphous-material properties, depending on the sample history, and occurring after the RESET operation, have gained currency: i) structural ageing [10]; and ii) mechanical-strain relief [11]. Amorphous (glassy) materials are non-equilibrium, metastable materials, and structural ageing of such rapidly-quenched materials to a lower-energy (but still amorphous) state is well-known. Hence, it is feasible that this structural-relaxation process might also involve the annealing out of structural defects which could give rise to electronic trap states in the bandgap in *g*-GST [10, 15-20]. This approach has been applied to the model of Poole-Frenkel conduction in *g*-GST, and the resistance drift has been ascribed to a concomitant decrease in carrier trap density [10, 15-20]. Recently, there have been a number of *ab initio* and classical-potential molecular- dynamics studies of ageing in the PCRAM material, *g*-GeTe [30-32], which have revealed that ageing causes structural changes, for instance relating to structural defects giving rise to electronic states with energies in the region of the bandgap. In particular, Ge-Ge homopolar bonds, associated with tetrahedral Ge configurations, appear to be annealed out, accompanied by a transformation of 2-fold Te sites to 3-fold Te configurations. Thus, the modelled *g*-GeTe material appears to transform towards a 3:3 structure, reminiscent of the corresponding crystal, on ageing. However, this picture of an ageing-induced reduction of gap-state defects, associated with homopolar Ge-Ge bonds, obtained from simulations, seems to be at variance with experimental glancing-incidence EXAFS data, where an *increase* in the Ge-Ge defect concentration was observed with ageing in thin films of as-deposited amorphous GeTe [33].

However, a widening of the electron-mobility bandgap with ageing is also evidenced from the simulational studies of *g*-GeTe [30-32]. This behaviour appears to be experimentally observed generally for all PCRAM materials [23-27], and indeed it has been claimed that an ageing-induced increase of the bandgap, and hence of the electrical-conductivity activation energy, E_σ, is solely responsible for the resistance-drift effect in *g*-GeTe and GST [26]. However, in the doped Sb_2Te PCRAM material, $Ag_4In_3Sb_{67}Te_{26}$ (AIST), the apparent increase of E_σ inferred from the resistance drift is four times *less* than the actual ageing-induced widening of the bandgap [26], implying that an increase of

the bandgap in the glassy state with ageing cannot be a universal mechanism for resistance drift.

An alternative extrinsic model for resistance drift also focuses on structural ageing, but instead concentrates specifically on the time-dependent relaxation of the elastic compressive strain induced in the *g*-phase in a PCRAM cell after RESET, as a result of the ~5% density difference between *c*- and *g*-phases of GST [11]. This strain is assumed to affect the bandgap, and hence the electrical resistance, of the material [11]. The local atomic motions, responsible for this structural relaxation, have been described by the phenomenological double-well potential (DWP) model [34]; a very broad (e.g. flat) distribution of activation barriers between DWPs is assumed to be responsible for the very broad, logarithmic time response of the resistance drift [14]. In this picture, defects with the lowest activation barriers for structural relaxation relax first. Recently, a different picture for the energetics of structural relaxation has been proposed [27], in which relaxation is presumed to be a collective, repetitive process, wherein a *single* activation energy (rather than a (flat) distribution of energies) characterises the relaxation process at any moment in time; this activation energy is then assumed to vary with time during the ageing process [27]. The structural relaxation was then connected to the Poole-Frenkel electrical-transport model to obtain the logarithmic time dependence of the resistance with time (eqn. 2), observed experimentally [27].

It has been shown that free-standing (i.e. presumably strain-free) *g*-GST nanowires can exhibit near-zero resistance drift [35], lending possible support for the strain-relaxation model. However, other work has shown that there is no change in the drift when the stress in *g*-GST films and memory cells is changed [36]. Earlier work [12] also showed that the drift process in cells appears to be reversible; after allowing drift to take place for a certain time, the drift process can be started again with the same dynamics following a voltage pulse, sufficient to cause electronic threshold switching but insufficient to produce a structural phase change, indicating, therefore, that the strain mechanism may not be dominant.

In summary, as noted by Noé et al in their extensive recent review on PCRAM [5], very different, and sometimes opposing, mechanisms have been proposed to account for the resistance drift: i) an increase [37] or decrease [17, 24] of disorder during drift; ii) an increase [12] or decrease [14] of the defect density during drift; iii) drift affected [35] or not affected [36] by mechanical stress. Thus, it can be safely concluded that the resistance-drift mechanism is still not understood and remains highly contentious.

There appear to be only two studies in the literature so far where the mechanism of resistance drift has been ascribed purely to an *electronic* mechanism, rather than being caused by atomic-relaxational effects. In the first such study, by Pirovano et al [12], it was assumed that negative effective-correlation-energy, valence-alternation-pair (VAP) defects exist in glassy PC materials, e.g. *g*-GST, namely C_3^+ and C_1^-, where C refers to a chalcogen atom (Te in this case), and the superscripts and subscripts refer, respectively, to the charge state and coordination number of the defects [38]. After a threshold-voltage switching pulse, it was assumed that these acceptor and donor states become filled with

carriers, creating unstable C_3^0 centres [39, 40]. The subsequent decay of these metastable filled states caused by electron transfer between defects, back to the stable C_3^+ and C_1^- centres, was then assumed to cause a time-dependent movement of the Fermi level back towards midgap, thereby causing the resistance drift as a result of the corresponding change in resistivity activation energy [12, 32]. However, the VAP model [38], based on the stability of oppositely-charged over- and under-coordinated chalcogen point defects, C_3^+ and C_1^- (the charges being relative to those of uncharged defects, C_3^0 and C_1^0, and of the 2-fold coordinated state of normally bonded chalcogens, C_2^0) appears not to be valid in telluride-based materials, such as *g*-GST or GeTe, where the *normal* chalcogen (Te) atomic coordination number appears to be nearer to three [4]. Moreover, the structural defects in the PC material, *g*-GeTe, manifested in classical-potential molecular-dynamics [31, 32] and *ab initio* molecular-dynamics (AIMD) simulations [30], and in *g*-GST evidenced by AIMD simulations [41] and a combined machine-learned ('GAP') potential and AIMD study [42], are not the simple VAP point defects envisaged in the D^+-D^- model [38]. Instead, the atomic configurations associated with defect gap states in *g*-GeTe and GST involve the cations (Ge) rather than the anions (Te). They are also not point defects, but tend to be more spatially extended, e.g. involving homopolar Ge-Ge bonds in short linear chains [31] in *g*-GeTe, or clusters of defective configurations of atoms, wherein the central Ge atom has a defective octahedral-like (defective-crystal-like) environment [42]. The energies of the electronic states associated with such Ge-centred structural defects in a series of models of *g*-GST were found to lie either close to the bottom of the conduction band or to lie near mid-gap [42]. These mid-gap states were found to be electron traps; occupation of such gap states by an electron caused the energy levels to shift down towards the valence band by ~0.3 eV [42].

The second report of an electronic mechanism for resistance drift is by Khan *et al* [43]. This includes resistance-drift data in *g*-GST measured at cryogenic temperatures to room temperature (125 – 300 K), for times in the range 10 – 10^4 s following a reset voltage pulse, and which are very similar to those previously measured at or above room temperature. The measured drift coefficient, υ, increases linearly with temperature, by about 100%, in this temperature range. However, it was found that there was a very significant illumination-induced change in resistance during the drift period on switching on/off a white LED; a very fast decrease in resistance was observed on switching on the light, followed by a very slow rate of decrease during illumination, and equivalently a very rapid increase in resistance on switching off the light, followed by a slower rate of increase during the unilluminated period. Moreover, the drift in resistance in the 'off' state ($\upsilon = 0.092$) was much greater than in the illuminated 'on' state ($\upsilon = 0.049$). It was argued on the basis of these results that, because resistance drift also occurs at low temperatures, it cannot result from structural relaxation since thermal-activation effects would be very much smaller than at room temperature or higher, and therefore it must have an electronic origin. In addition, the very large decrease of the drift coefficient, υ, by a factor of ~2, on illumination also supports an electronic, rather than an atomic-relaxational, origin for the resistance drift. The light-induced fast response in resistance was attributed to photo-generated carriers, while the much slower changes suggest the presence of slow

trap-to-trap transitions, similar to those that can give rise to phosphorescence observed in high-trap-density materials [43].

2. An electronic model for resistance drift

In this paper, an alternative intrinsic electronic mechanism is proposed for the origin of the resistance drift in PC materials, which does not depend on ageing-induced structural relaxation. This is based on the well-established notion that there can exist spatially localized trap states for charge carriers in the bandgap of amorphous/glassy semiconductors, due to structural disorder (defective and topological) [44], as found in simulations of GST [42]; it does not assume that structural or strain relaxation is responsible for the resistance-drift effect.

The effective resistance of a two-terminal PCRAM cell in a given (e.g. RESET) state as a function of time, $R(t)$, can be ascertained by measuring the current $I(t)$ at sequential times using a series of constant, low-voltage (non-perturbing) read pulses, V_{read}, i.e.:

$$R(t) = V_{\mathrm{read}}/I(t). \tag{2}$$

Thus, the *upward* drift of resistance with time inferred to be observed in PCRAM materials such as *g*-GST (eqn. (1)) can be due to a *decrease* in the measured current, $I(t)$, with time for a fixed V_{read}. This behaviour is very reminiscent of the long-time photocurrent decay (LTPD) from the photoconductive steady state for constant illumination, having a power-law dependence, $I_{\mathrm{PC}}(t) \sim t^{-\upsilon}$, which has been observed in, say, hydrogenated amorphous silicon, *a*-Si:H, extending over decades in time, up to at least 10^4 s [45, 46]. In fact, this ‘persistent photoconductivity’ (PPC) behaviour, with a power-law time decay, is rather widespread, having been observed in systems as varied as, for example, GaN-based Schottky diodes [47] and nano-crystalline TiO_2 films [48]. However, the phenomenon should be distinguished from the *transient* photocurrent decay (TPD) occurring after *pulsed* optical excitation, in e.g. amorphous semiconductors, where the decay is over much shorter times; this latter behaviour has been interpreted in terms of multiple trapping of excess carriers in (exponentially energetically-distributed) band-tail states [49, 50]. This type of behaviour could be responsible for the very-short-time increase in resistance evident in GST immediately after the reset pulse [13], or the very rapid increase in resistance observed in *g*-GST after cessation of light illumination [43]. In contrast, LTPD/PPC in amorphous semiconductors has been ascribed to the slow release of electrons and/or holes from traps over a long period of time, leading to subsequent recombination with excess charge carriers and hence a decrease of the photocurrent [45, 46]. In GaN, this process affects the Schottky barrier height [47], and in nano-crystalline materials, it is controlled by charge-dependent potential barriers at interfaces [48].

However, there is a key difference between (voltage-pulse-induced) resistance drift in *g*-GST and the long-time photocurrent decay observed in other disordered semiconductors, since glassy GST is made in a unique way in PCRAM cells. Instead of simply quenching

a vapour to form an amorphous material, or quenching a liquid, formed by the external thermal melting of a crystal, as for normal glass formation, the thermal energy for melting the memory material in a PCRAM cell is provided *internally* by the Joule heating associated with the application of a RESET voltage pulse. The *I-V* characteristics of GST are non-linear (non-Ohmic), markedly so for the glassy phase, where threshold switching is observed at a threshold voltage, V_{th}, with an *'S'*-like *I-V* characteristic [39, 40], but they are also non-linear for the crystalline phase [51]. This non-Ohmic increase in current is due to electric-field-assisted carrier-generation processes, such as impact ionization [39, 40]. Thus, when the glassy phase of GST forms, on quenching from the liquid in a PCRAM cell, it is in the presence of a very high electron-hole current density produced by a RESET pulse. Hence, it is reasonable to assume, therefore, that, under such conditions, most of the localized gap-state trapping centres, characteristic of disordered materials and created during the formation of the *g*-GST phase, become filled with electrons and holes during the RESET process itself [52]. Thus, the electronic condition of *g*-GST immediately post-RESET is equivalent to that pertaining in, for example, *a*-Si:H just after the cessation of steady-state *optical* excitation and prior to the subsequent occurrence of LTPD/PPC [45, 46].

It is proposed here that long-time thermal detrapping of charge carriers (e.g. electrons) resulting from the RESET process leads to their recombining with the thermally-generated charge carriers (mainly holes in the valence band for these p-type materials) which contribute to the measured current in a PCRAM device, and that this effect can therefore be responsible for the time-dependent apparent drift in resistance observed in these materials. The electrical conductivity of a (p-type) material can be written as:

$$\sigma = pe\mu_h = l/RA, \tag{3}$$

where p is the concentration of mobile holes, e is the electronic charge, μ_h is the hole mobility (assumed to be constant), l is the sample length and A its area, and R is the sample resistance. Thus, a time-dependent decrease of the conducting-hole concentration, p, due to recombination with detrapped electrons, leads to a decrease in the conductivity, or equivalently an increase with time of the measured resistance, R, i.e. resistance drift. If the mobile-hole concentration, and hence the current, decays as $p \propto I \sim t^{-\upsilon}$, then, according to eqns. (2, 3), the resistance will increase (drift) with time as $R \sim t^{\upsilon}$.

It has been widely observed that the SET (crystalline) state of GST does *not* exhibit resistance drift [13, 15, 18]. It is proposed that, in the context of the detrapping/ recombination model for resistance drift in *g*-GST (and other PCRAM materials) proposed in this paper, this difference in behaviour is due to the (metastable rocksalt) *c*-phase of GST *not* having deep-lying, spatially-localized gap states that can act as slow-release trapping centres. The traps that are most likely to occur in *c*-GST, namely acceptor-like Ge/Sb atomic vacancies on the cation sub-lattice of the rocksalt-like structure (commensurate with the cation-poor compositions of GST PC materials, such as $Ge_2Sb_2Te_5$ [4]), are believed to lie at the top of the valence band, thereby accounting for the degenerate p-type behaviour of this material [52, 53]. It has been shown [54] that cation vacancies in crystalline materials (e.g. in Cu_2O) tend to give rise to delocalized,

conductive states, whereas anion vacancies can produce localized non-conductive states. The PPC behaviour observed in crystalline II-VI and chalcopyrite materials has been ascribed to electron trapping by such localized *anion* vacancies [55], and thus PPC should not occur in *c*-GST containing cation vacancies. Siegrist et al [53], however, have suggested that, on the basis of a change in the temperature coefficient of resistivity (TCR) of GST with increasing annealing temperature through the metastable-rocksalt to stable-hexagonal crystal-crystal phase transition, localized band-tail states may exist in the rocksalt phase of *c*-GST due to Anderson localization associated with randomly-distributed cationic vacancies. (However, percolation effects in the two-phase system, or countervailing temperature dependences of carrier concentrations and mobilities in the mixed electron-hole conducting system, may also contribute to the observed TCR behaviour.) In any case, it is generally believed that *c*-GST does not contain *deep* localized states that could control the recombination, and hence determine the measured current, over long time-scales. Hence, this model predicts that PCRAM materials in the crystalline SET state should *not* exhibit resistance drift, as is experimentally observed.

Although most reports of resistance drift in PCRAM materials have been for materials in the glassy (RESET) state, as described above, nevertheless there are a very few reports of resistance drift being observed in the *as-deposited* amorphous, rather than the melt-quenched (RESET) glassy, state, e.g. for GST, GeTe and doped Sb_2Te (AIST) [22, 24]. However, such resistance-drift measurements were performed on as-deposited amorphous films of materials subjected to elevated-temperature annealing conditions, e.g. at temperatures between 50 and 80 ^{o}C [24]. Thus, under such annealing conditions, it is very likely that annealing-induced, atomic-relaxational effects are responsible for the resistance drift. Thus, the electronic mechanism proposed in this paper relates only to the glassy, melt-quenched (RESET) state of a phase-change material, particularly for ambient temperatures and below.

3. Discussion

A number of models have been proposed to account for the time-dependent (power-law) behaviour of LTPD/PPC [45, 46]. Hence, by inference, and on the basis of the model proposed in this paper, they can also be considered to explain the resistance drift in *g*-GST (eqn. 1). The LTPD/PPC observed in undoped n-type *a*-Si:H involves electron transport, and hence electron trapping or hole-limited recombination processes need to be considered [45, 46]. However, PCRAM materials, in both *c*- and *g*-states, are generally p-type, like most other chalcogenide materials, and therefore electrical conduction is governed by hole transport instead [4]. Thus, one can simply take over the analysis given in [46], reversing the roles played by electrons and holes.

One possible mechanism for a time-dependent decay of the hole concentration or current is recombination of non-equilibrium charge carriers [46]. In the case of strong (monomolecular) recombination, where retrapping is negligible, the decay of the hole concentration/current after the reset pulse can be limited by thermal emission of trapped holes. For the case of a uniform distribution of traps, it can be shown that [46] $R \sim t^{1}$, and for an exponential distribution of (tail-state) traps [46], $R \sim t^{(1 + T/T')}$. Both these scenarios

give rise to a drift coefficient with a value very different ($\upsilon \geq 1$) from that observed experimentally ($\upsilon \sim 0.1$). For the case of bimolecular recombination [46], $R \sim t^1$. So this mechanism does not account for the resistance-drift behaviour observed in g-GST, either.

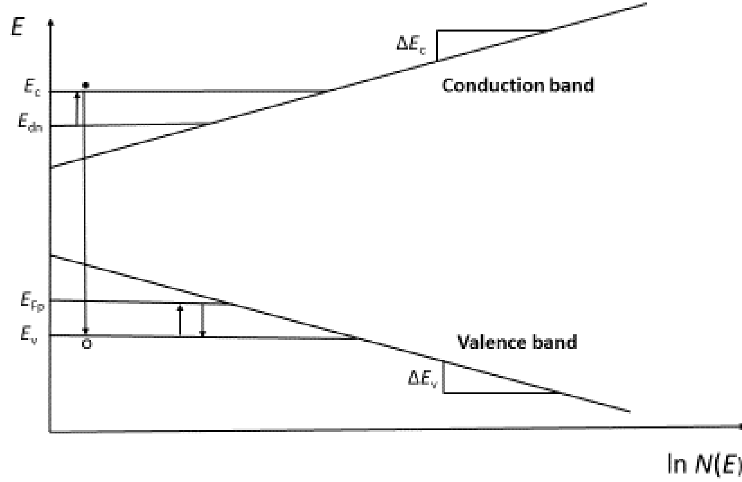

Fig. 1 Illustration of the charge-carrier trap-release and recombination model of the origin of resistance drift in the melt-quenched glassy state of phase-change memory materials. The exponential densities of valence-band (VB) and conduction-band (CB) electron states in the vicinity of the bandgap (eqns. 4, 5) are shown schematically, with the mobility edges, marking the extended/localized demarcation energies, being at E_c and E_v in the CB and VB, respectively. The quasi-Fermi level, E_{Fp}, for holes in quasi-thermal equilibrium, via release and retrapping events indicated schematically, and E_{dn} representing the time-dependent demarcation energy (eqn. 10) for electron emission, are superimposed on the density-of-states profiles. The electron-hole recombination process after electron emission is shown schematically.

Perhaps the most suitable approach is that of electron-emission-limited recombination [46]. It is assumed that trapped electrons need to be released to extended states lying beyond the mobility edge, e.g. from deep-lying traps in *g*-GST [42], before they can recombine with hole charge carriers (Fig. 1). For simplicity, electron and hole tail-state traps are assumed to be exponentially distributed in energy, as appears to be generally the case in amorphous semiconductors [44], i.e. respectively:

$$N_t^e(E) = N_0^e \exp[-(E_c-E)/\Delta E_c] \quad (4)$$

$$N_t^h(E) = N_0^h \exp[-(E-E_v)/\Delta E_v] \quad (5)$$

where E_c, E_v are the mobility edges in the conduction band (CB) and valence band (VB), respectively, and ΔE_c, ΔE_v (or equivalently [46], k_BT_c and k_BT_v , respectively) are measures of the widths of the band tails to the CB and VB, respectively (see Fig. 1). Simulation studies indicate that deep electron-trap gap states can also exist in *g*-GST

which, upon trapping electrons shift in energy even further away from the CB edge [42]. In the case of weak recombination for holes, where a hole will experience many release and retrapping events in shallow VB band-tail states before recombining, the holes are in quasi-thermal equilibrium and their occupancy is determined by a quasi-Fermi level, E_{Fp}. Thus, the densities of free and trapped holes can be written respectively as:

$$p = k_B T N_0^h \exp[-(E_{Fp}-E_v)/k_B T] \quad (6)$$

$$p_t = \Delta E_v N_0^h \exp[-(E_{Fp}-E_v)/\Delta E_v] \quad (7)$$

$$\text{i.e.} \quad p \sim p_t^{1/\gamma}, \quad (8)$$

where $\gamma = k_B T/\Delta E_v$. The occupancy of electron traps is assumed to be determined by thermal emission of electrons; retrapping is assumed to be negligible. In this case, the density of trapped electrons is given by:

$$n_t \sim \Delta E_c N_0^e \exp[-(E_c-E_{dn})/\Delta E_c], \quad (9)$$

where the time-dependent electron demarcation energy, E_{dn}, is given by [49, 50]:

$$E_{dn} = E_c - k_B T \ln(\upsilon_0 t) \quad (10)$$

and υ_0 is an attempt-to-escape frequency, assumed to be constant for all trap depths. Eqn. 10 is the origin of the very wide time domain during which resistance drift can occur in this model. Substituting eqn. (10) into (9) gives:

$$n_t \sim \Delta E_c N_0^e (\upsilon_0 t)^{-\beta} \quad (11)$$

where $\beta = k_B T/\Delta E_c$. It is assumed that all traps are filled immediately after RESET; charge neutrality dictates that $n_t = p_t$. Thus, from eqns. (8, 11):

$$p \sim p_t^{1/\gamma} = n_t^{1/\gamma} \sim t^{-\Delta E_v/\Delta E_c} \quad (12)$$

and hence, since $p \sim I \sim R^{-1}$ (eqn. 3), it is predicted that the resistance should therefore increase (drift) with time, behaving as:

$$R(t) \sim t^{\Delta E_v/\Delta E_c}. \quad (13)$$

Thus, comparison with eqn. (1) indicates that the resistance-drift exponent is given by:

$$\upsilon = \Delta E_v/\Delta E_c. \quad (14)$$

In the special case that $\Delta E_c > k_B T > \Delta E_v$, the maximum in the energy distribution of excess holes just after RESET is near E_v, i.e. $p >> p_t$, and the condition for charge neutrality therefore changes to $p = n_t \sim t^{-k_B T/\Delta E_c}$ (see eqn. 11), so that now the resistance-drift exponent becomes:

$$\upsilon = k_B T/\Delta E_c. \qquad (15)$$

In this latter case, therefore, the resistance-drift coefficient should increase linearly with temperature. However, even the apparently temperature-independent exponent in eqn. (14) may in fact be somewhat temperature-dependent [25] if the band-tail densities of states (c.f. equations (4, 5)) are not accurately exponentially dependent on energy over a wide energy range, as assumed in the derivation of eqn. (13), especially over the energy range explored by the displacement of the electron demarcation energy (eqn. (10)). An approximately linear dependence of the drift exponent, υ, with read temperature (as opposed to annealing temperature [10, 16]) has been reported experimentally for PCRAM materials [33, 43], in accord with this prediction.

4. Conclusions

In conclusion, it is proposed here that the phenomenon of the time-dependent increase (drift) in resistance observed in the melt-quenched glassy (RESET) state of phase-change memory materials, such as Ge-Sb-Te alloys, and which threatens the future of multi-bit storage, multilevel-programming operation in phase-change random-access memory (PCRAM) technology, can be electronic in origin and can be regarded in the same way as the persistent-photoconductivity phenomenon widely observed in disordered semiconductors. This behaviour can be understood in terms of a mechanism involving slow charge-carrier detrapping and subsequent recombination following electron-hole injection during the RESET pulse; this is determined by the energy widths of the band-tail electronic densities of states of the PCRAM material. A similar mechanism has been invoked previously to describe the long-time photocurrent decay exhibited by amorphous semiconductors, such as amorphous (hydrogenated) silicon. Structural (atomistic) ageing effects are not involved. Hence, resistance drift could be mitigated, in principle, in the glassy state of PC materials if, by using suitable material engineering, the extent of valence-band tailing could be reduced. This would thereby facilitate multistate memory operation, leading to higher future data densities for PCRAM.

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