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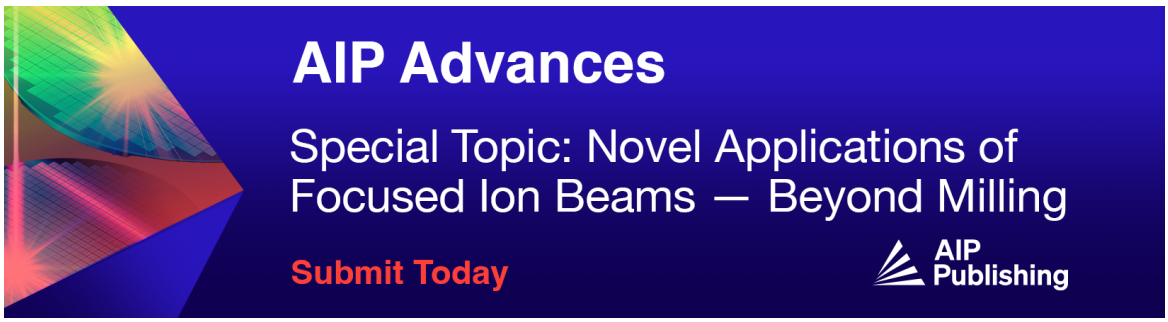

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Mixed phase $Ge_2Sb_2Te_5$ thin films with temperature independent resistivity

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The electrical properties of polycrystalline $Ge_2Sb_2Te_5$ thin films containing both the metastable *fcc* phase and the stable *hcp* phase have been studied. The resistivity and its temperature dependence have been modelled using effective medium approximation. By varying the volume fraction of the two phases it is possible to get films with different resistivities and temperature coefficient of resistance, changing without discontinuity from negative (*fcc*) to positive value (*hcp*). Mixed phase films with resistivity almost independent of the temperature are obtained at about 4 mΩ cm. [http://dx.doi.org/10.1063/1.4775351]

I. INTRODUCTION

Very precise high resistance values, stable over a large temperature range, are often required in microelectronics, especially for high precision analog devices, such as, for example, operational amplifiers or voltage references. Thin film resistors, with thickness of a few nanometers, are usually employed for this purpose. The most commonly adopted materials are TaN,[1] SiCr alloy[2] or cermet alloys based on Cr, Si, B and SiC.[3]

In order to get resistors almost independent of the temperature, materials with temperature coefficient of resistance (TCR) less than 100 ppm/K are preferred. Several solutions have been proposed for this purpose, such as series- or parallel-connected resistors of different materials having different TCR and, more precisely, positive TCR and negative TCR matched together so that the effective temperature coefficient is almost zero.[4] As an example, one of the most widely employed material for thin film resistors is a Si:Cr:SiC based alloy, with a microsctructure characterized by Cr rich metallic clusters, with positive TCR, embedded into an amorphous semiconductive matrix, with negative TCR.[3,5] By optimizing the composition, TCR values close to zero can be obtained.

Even with very well controlled processes, however, the value of initially fabricated thin film resistors typically falls within a 3-15% range of tolerance. Therefore to get more accurate and stable values a subsequent trimming operation can be required. This is usually done by physically removing or modifying portions of the resistor through the use of an appropriate laser (laser trimming)[6] or by other electrical methods, such as electrical fusing, self-heating[7] or heater resistors,[8] offering the advantage to adjust also shifts due to packaging.

In this letter we show that phase change materials, and in particular $Ge_2Sb_2Te_5$ thin films containing two crystalline phases, can be employed to obtain resistors almost independent of the temperature, for high precision applications.[9] The resistivity value of these mixed phase films is such that trimmable resistors can be fabricated with thickness in the range of some tens of nm, far more viable from a point of view of the device fabrication.

A particularly intriguing aspect of this resistivity value is that it is close to the limits of metal-insulator transition. This circumstance has led to the proposal that the reason for the observed zero

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TCR in such chalcogenide alloys ($GeSb_2Te_4$) is an order-disorder transition.[10] In this letter we show that in $Ge_2Sb_2Te_5$ the zero TCR, on the contrary, can be well explained by the co-existance of two crystalline phases.

Phase change materials are characterized by marked variations of the electrical and optical characteristics upon phase transitions. Reversible phase transitions may be obtained by heating and/or melting, for example, using laser or electrical pulses. Thanks to these characteristics, phase change materials have been extensively studied in the last years for memory applications, initially for optical memories (cd-ROM and DVD),[11] and more recently for nonvolatile memories.[12]

$Ge_2Sb_2Te_5$ (GST) is one of the most common compositions. It is a polymorphic material, exhibiting two crystalline phases. The metastable phase, formed at temperatures around 130-200°C, has a face centred cubic (*fcc*) structure and it is used for memory applications. At higher temperatures (around 400°C) the *fcc* converts into the stable hexagonal *hcp* structure.

It has been reported in literature that the electrical properties of these two crystalline phases as a function of temperature have an opposite trend: the *fcc* phase exhibits a decrease of resistance versus temperature, typical of semiconductor materials, while the resistance of *hcp* phase increases with increasing temperature, thus behaving like a metal.[10,13]

As it will be shown, this property enables a new application of phase change materials, since mixed phase GST films can be employed to obtain resistors almost independent of the temperature. The possibility to rapidly and reversibly change the phase of the material through laser pulses or electrical pulses is a further advantage for applications as high preciosion resistors, since it allows finely trimming of both the resistance and the TCR.

II. EXPERIMENTAL

For this study 100 nm thick GST films were deposited over Zn-SiO_2, and covered by 5 nm of Zn-SiO_2 to protect the surface from oxidation and evaporation. Si (100) wafers have been used as substrate and the phase change material was deposited in the amorphous phase. The electrical properties of GST films have been studied through in situ four point probe resistance measurement during annealing. The films were heated at constant ramp rate, up to 650 K or 670 K and then isothermally annealed at the maximum reached temperature for different annealing times. In this way mixed phase samples have been obtained, containing both the metastable *fcc* phase and the stable *hcp* phase. After the annealing the temperature dependence of the resistance in mixed samples was measured in the temperature range 300-400 K.

The structure of the material has been investigated through X ray diffraction in grazing angle (0.7°), using a D6 Discover Bruker-AXS diffractometer equipped with a thin film optics. At the incident angle used, the penetration depth of the beam into the GST layer was reduced to ∼90 nm.

III. RESULTS AND DISCUSSION

Figure 1 shows as an example the sheet resistance versus temperature for two samples annealed at different ramp rates up to 670 K. The film, initially amorphous, exhibit a large resistance decrease at temperature between 450 and 500 K, depending on the heating rate. This first decrease corresponds to the formation of the metastable *fcc* phase. After the crystallization the resistance continues to decrease as a function of temperature. The steep resistance drop observed at 670 K represents the resistance decrease during the isothermal anneal. Samples annealed at 670 K were treated for different annealing times. The resistance measured during cooling is also shown. In both the cases after annealing the resistance linearly changes as a function of temperature, but with an opposite trend. In order to evaluate the temperature variation of the resistance after the annealing, the resistivity has been measured in the range 300-400 K. The resistivity versus temperature after annealing for all the studied samples has been reported in the inset of Figure 1. All of the samples exhibit a linear dependence of the resistivity versus temperature. Depending on the ramp rate, the annealing temperature and time, different resistivity values are obtained, with positive or negative slope.

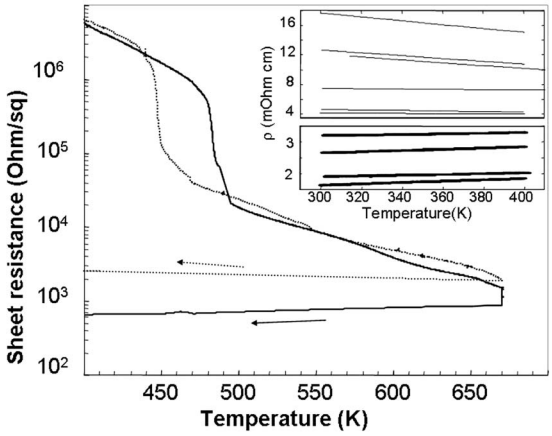

FIG. 1. Sheet resistance versus annealing temperature at two different ramp rates and annealing time @670 K. In the inset, the resistivity versus temperature, as measured after annealing, for all of the studied samples.

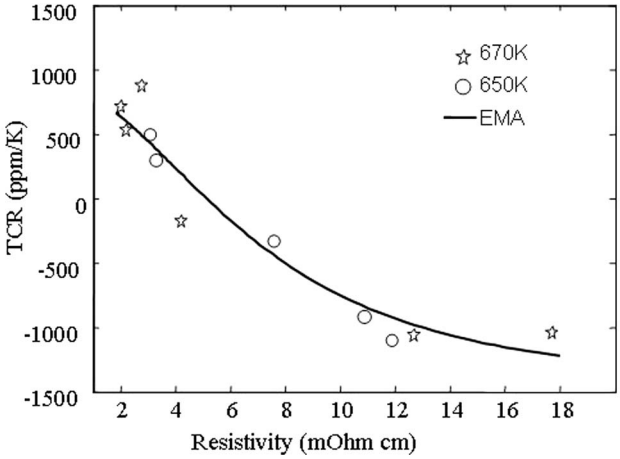

FIG. 2. Temperature coefficient of resistance as a function of the film resistivity, as measured in samples annealed up to 670 K (stars) or 650 K (circles) for different times. TCR has been obtained by linearly fitting the resistivity vs temperature in the range 300-400 K. Solid line has been obtained according to the effective medium approximation.

Films with resistivity larger that 10 mOhm cm exhibit almost the same negative slope. Samples with resistivity lower than 4 mOhm cm behave like metals, with resistivity increasing as a function of temperature.

In both the cases the resistivity data can be linearly fitted using the equation $\rho = \rho_0(1+\alpha\Delta T)$. The coefficient α is the normalized first derivative of the resistivity with respect to the temperature and is usually indicated as temperature coefficient of resistance. TCR values obtained by linearly fitting data in the inset of Fig. 1 are shown in Figure 2 as a function of resistivity. Circles and stars indicate samples annealed up to 650 K or 670 K, respectively. Although obtained at different ramp rates, annealing temperatures and time, the trend of the data can be reproduced according to the effective medium approximation (EMA), as will be detailed later on. The solid line in Fig. 2 has been obtained by following the EMA and employing the average experimental values.

The electrical properties have been related to the film structure by X ray diffraction analysis. Figure 3 shows the X ray diffraction patterns obtained for samples with different resistivity. In the film with the lowest resistivity only the stable *hcp* phase has been detected. As the resistivity increases, peaks corresponding to the metastable *fcc* phase appear, with increasing intensity.

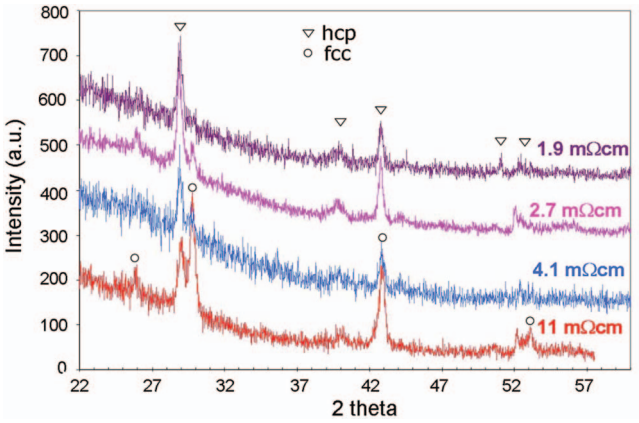

FIG. 3. X ray diffraction patterns of annealed samples, acquired for different resistivity values. Only the hcp phase is detected at the lower resistivity value. As resistivity increases, diffraction peaks corresponding to the *fcc* structure become more intense.

On the base of these results, the change of sign in the temperature dependence of the resistivity, characteristic of a metal-insulator transition (MIT), appears to be controlled by the formation of the stable *hcp* phase.

We have then related the electrical properties to the material structure by considering the effective medium approximation (EMA). This theory, first proposed by Bruggeman[14] and then, in a different context, by Landauer,[15] has been largely employed to describe macroscopically inhomogeneous media, i.e. materials in which physical parameters such as the conductivity, the dielectric function or the elastic modulus, vary in space. Considering a random mixture of two types of grains (*fcc* and *hcp*), present in fractions X and (1-X) and characterized by different conductivities σ_{fcc} and σ_{hcp}, the effective conductivity σ of the mixture can be calculated by assuming that each grain is immersed in a homogeneous effective medium of conductivity σ, which will be determined self-consistently. The self consistency condition required by the EMA is that the average electric field within a grain shall equal the electric field far from the grain. By using this approach, the well know equation is obtained:

$$X\frac{\sigma_{hcp}-\sigma}{\sigma_{hcp}+2\sigma}+(1-X)\frac{\sigma_{fcc}-\sigma}{\sigma_{fcc}+2\sigma}=0 \qquad (1)$$

This quadratic equation has two solutions. Only one is physically sensible and allows correct limiting behaviour for X → 0 or 1.

By using Eq. (1), the *hcp* fraction as a function of resistivity can be evaluated. By taking the first derivative of the resistivity with respect to the temperature, taking into account for the temperature dependence of the resistivity in the two phases, α_{fcc} and α_{hcp}, the TCR α in the mixed phase can be also evaluated.

Figure 4(a) and 4(b) show the resistivity as a function of extracted *hcp* fraction, according to EMA, and the TCR of the mixed phase as a function of the *hcp* fraction, respectively.

The *hcp* volume fraction has been also independently evaluated by X ray diffraction data and reported in Fig. 4(a) as crosses. The agreement between diffraction data and the estimation according to the EMA is quite good.

Solid lines shown in Fig. 2 and in Fig. 4 have been obtained by using the experimental values of the resistivity for the pure *fcc* and *hcp* phase, as well as the experimental value of the TCR in the two phases, α_{fcc} and α_{hcp}.

The interesting consequence is that it is possible to get a material with resistance almost independent on the temperature (TCR ≈ 0), at a given *hcp* fraction. Such a value in our sample corresponds to about 40% of *hcp* volume fraction.

The change of sign in the TCR upon annealing has been reported for several Ge:Sb:Te alloys with composition along the pseudobinary line connecting GeTe to Sb_2Te_3 in the ternary phase

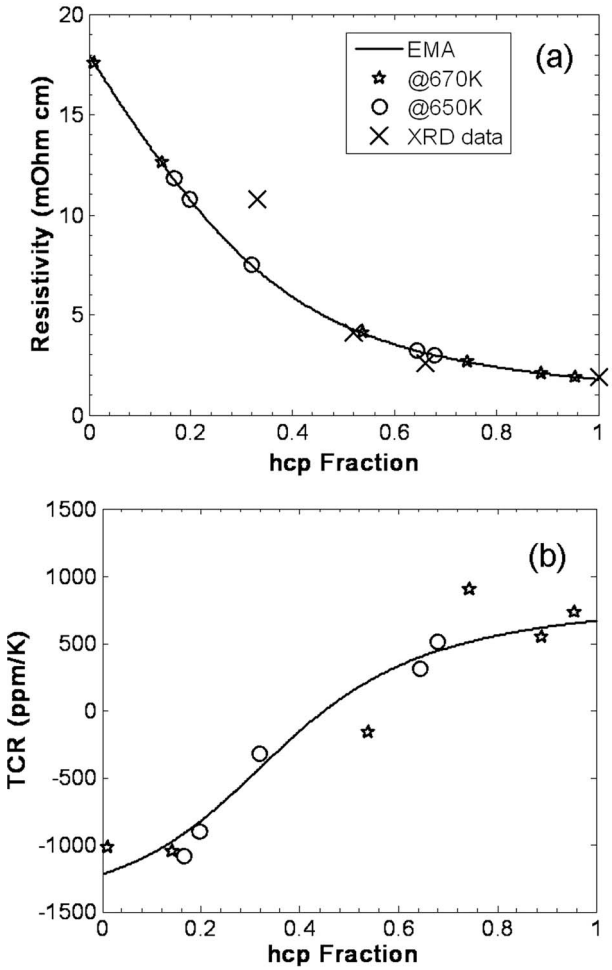

FIG. 4. (a) Measured resistivity as a function of *hcp* volume fraction, obtained according to EMA. Experimental values of *hcp* fraction, obtained from XRD data have been also reported for comparison. (b) TCR versus *hcp* fraction. Solid line is the theoretical TCR value, as obtained by taking the first derivative of resistivity in the effective medium approximation. values.

diagram. In particular, in $GeSb_2Te_4$ it has been recently observed the existence of a metal-insulator transition,[10] separated by the structural *fcc-hcp* transition. This has been explained as an effect of an order-disorder transition, according to the Anderson model.[10]

By following the Ioffe Regel criterion,[16] in Ref. 10 the maximum resistivity for a metal ρ_{max} in $GeSb_2Te_4$ has been evaluated to be 2.3 mOhm cm. The same calculation can be done also for $Ge_2Sb_2Te_5$. By using carrier concentration reported in literature for the GST hexagonal phase[17] (2.7×10^{20} cm^{-3}), a value of $\rho_{max} = 2.4$ mOhm cm is obtained.

The resistivity of the metallic *hcp* phase, measured in the samples we studied, is 1.8 mOhm cm, just below the maximum value expected for the material to be a metal.

However, the resistivity at which we have observed the minimum TCR (4 mOhm cm), although quite close, is different from ρ_{max}, at which the metal-insulator transition would have been observed in the case of an order-disorder transition, without the structural *fcc-hcp* transformation.

This observation is strongly supported by the diffraction data, where both the phases are detectable. Moreover, assuming the contribution of the *fcc* and *hcp* phases, both the resistivity and its temperature dependence (TCR) can be fairly reproduced employing the EMA, over a wide range of sample preparation conditions (ramp rate, annealing temperature and time).

These results therefore suggest that the zero TCR in GST is determined by a particular *hcp/fcc* volume fraction, at which the positive dependence of the resistivity versus temperature of the

hcp phase is almost completely compensated by the negative dependence of the resistivity versus temperature in the metastable *fcc* phase.

The volume fraction at which the minimum TCR is reached is dependent on the resistivity and the TCR values α_{fcc} and α_{hcp} of the two phases exhisting in the mixture. Therefore, for other phase change materials with different compositions, also exhibiting two crystalline phases with opposited trend of TCR, the minimum TCR value can be obtained at different *hcp/fcc* volume fractions.

In GST we have seen the minimum TCR corresponds to an effective resistivity of the mixed phase material of about 4 mOhm cm. Such a value is quite promising for the proposed application as high precision resistors. Indeed, high resistivity values are generally preferred, in order to save space. However, it is more difficult to get low TCR values together with high resistivity using thin film materials, since the film thickness is usually so low so that cannot be further reduced. On the other hand, increase of the resistivity by changing the material composition would reduce the metallic fraction and therefore lead to higher negative TCR values.[5]

By using GST films with resistivity around 4 mOhm cm, sheet resistance values of 2 kOhm/square could be easily obtained with a very low TCR, at thickness much more viable than the few nm usually employed by thin film resistors.

Therefore, GST in the mixed *fcc-hcp* phase can be a valuable candidate for precision resistors, with tunable TCR. Moreover, the possibility to rapidly change the resistivity of GST by laser or electric pulses represents a further advantage in the use of phase change resistors as trimmable devices for high precision applications and, in general, for the development of analogical reconfigurable electronic devices.

IV. CONCLUSIONS

In conclusion, we have shown that $Ge_2Sb_2Te_5$ during the transformation from the metastable *fcc* phase to the stable *hcp* structure undergoes a continuous change of conductive properties from insulator to metal. The mixed phase resistivity and its temperature dependence can be well reproduced according to the effective medium approximation. For a given *hcp* fraction, together with the resistance value, also the temperature coefficient of resistance can be predicted.

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