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DIFFUSION KINETICS IN GOLD-AMORPHOUS GeTe₄ THIN FILMS

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ABSTRACT - The main processes which occur during the gold fast diffusion into amorphous GeTe₄ films are followed by RBS measurements, for annealings carried out at temperatures below Tg (140°C). From the profiles obtained, strikingly similar to grain-boundary (G.B.) profiles, we extract: the diffusion coefficients for low-concentration kinetics using specific G.B. theories. Then we present a model based on recent trends in amorphous structures. This model is also consistent with experimental data obtained from complementary characterizations as electron microscopy X-ray and transport properties.

INTRODUCTION - In earlier papers [1,2] we reported on the electrical degradations kinetics induced by the metal electrode diffusion. The observed low-temperature fast-diffusion exhibits unusual kinetics changes associated with the temperature rise. In this paper we should like to present and discuss new results on the diffusion processes initiated by air or vacuum annealings. Knowledge on the metal-amorphous thin couples diffusion is necessary indeed to improve the reliability of amorphous devices.

EXPERIMENTAL - The diffusion couples are elaborated in a RF multitarget diode sputtering system. The final thicknesses of the deposits, from 0.14 to 1.1 µm of GeTe₄ from 100 Å to 450 Å of gold, are controlled using Tencor apparatus. After air or vacuum isothermal annealings at Room Temperature (RT), 80°C, 100°C and 120°C, samples are then analysed by He-ion R.B.S. in the 3.7-8 MeV energy range.

Further investigations are carried out by X-ray diffraction of diffusion studies as well as electrical resistivity measurements, all supported by TEM or SEM observations.

DIFFUSION RESULTS - The profiles obtained from thick (1.1 µm GeTe₄) configurations (fig. 1F) clearly display G.B.-depth dependance. So we use in this part appropriate classical polycrystalline diffusion models and notations.

For bulk GeTe₄ and in this temperature range, the volume diffusion coefficient (Dᵥ) is nearly negligible and in no case can explain the high gold-concentration levels reached in our films. That is why we adopt the Whipple-based "defect-enhanced" diffusion formalism (fig. 3a) in which the solute migrates from G.B. through regions with high density of defects characterized by the pseudo-lattice diffusion coefficient D'ᵥ [3]. Assuming an infinite value for the boundary diffusion coefficient (Dᵥ) one gets flat G.B. profiles. The "plateau rise" rate, following a t₀.5 law, gives the D'ᵥ expression: D'ᵥ = K C²/t where K is a geometrical factor and C the plateau concentration. Thin couples (1400 Å/400 Å) are specially designed in order to give a better adjustment to the Dᵥ infinite condition, so we obtain for air and for vacuum annealings:

Air: D'ᵥ = 4.6 x 10⁻¹⁰ cm².s⁻¹  Q'ᵥₐ = 0.55 eV
Vacuum: D'ᵥ = 7.5 x 10⁻⁷ cm².s⁻¹  Q'ᵥᵥ = 0.75 eV

For gold concentration above 10 at.% the model is no longer appropriate, since the time dependance then starts to decrease (fig. 4).
According to Gilmer and Farrell's thin films formulation [41], we obtain the real values for G.B. diffusivities (fig. 2):

Air: $k_0 D_{b_A} = 2.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
$\Theta_{b_A} = 0.7 \text{ eV}$

Vacuum: $k_0 D_{b_V} = 1.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
$\Theta_{b_V} = 0.55 \text{ eV}$

Figure 1 - Gold diffusion profiles in amorphous GeTe$_4$ thin-films. The curve F is obtained for a thicker configuration.

Figure 2 - Arrhenius plots of "defect-enhanced" (D') and Gilmer and Farrell's GB diffusion coefficients. (a, c): vacuum anneals; (b, d): air anneals; (- - -): extrapolated data from our low-T resistivity measurements.

Figure 3 - a) Polycrystalline "defect-enhanced" diffusion processes. b) Amorphous corresponding processes in our "globular" model, including formation of the c-AuTe$_{1.7}$ compound.

DISCUSSION - The previous values must be related to a system free of structural changes, as grain growth or phase transition: that indeed occurs during the 0.5 low-concentration dependance, dependance confirmed by the electrical measurements (fig. 6a).

Now the problem is how to connect that crystalline point of view with the amorphous situation. That is achieved by the proposed model summarized in the fig.3b.
The main features of this model consist in three basically different competing mechanisms.

a) A first very fast diffusion \( D_b \) fills the intergranular or intercolumnar (interglobular) spaces (fig. 7a,b,c) for which a general agreement seems to exist\([5,6,7,8]\). In our case, the mean size of these observed structures is close to \( L = 300 \, \AA \), this value being used for numerical calculations\([3]\). At R.T., only this process occurs, as shown by the flat profile (c) in fig. 1 and leads to a mean solute concentration about 5 at.%. This value can be significantly reduced by structural thermal relaxation before gold deposition.

b) The secondary, somewhat slower, easy-path diffusion is equivalent to a \( D'_2 \) called \( D'_{\text{open porosity}} \) and fills up to \( \approx 10 \, \text{at.\%} \) without any X-ray evidence for phase transitions (fig. 4 : \( T = 80^\circ\text{C} \)). It takes place in the large high-stressed regions located in the "globular" regions. In a recent paper, Phillips \([5]\) describes these regions as including a more or less connected network of porosities. In our case, the tendency of Te atoms to easily segregate at surface surely contributes to make those porous regions Te-rich. RBS studies of the oxygen profile evolution during air or vacuum anneals show that this element, preferentiallysituated at the two perturbed interfaces, also diffuses noticeably from the "heart" of the film. A "de-screening effect" due to the departure of oxygen atoms from those Te-rich (in fact Te-O rich) regions may explain that the vacuum-kinetics are faster than the air ones by an order of magnitude (fig. 2).

c) Lastly, at concentrations above 10 at.%, a multiphase diffusion \( D_{\text{vac}} \) occurs when detectable amounts of the non-equilibrium lacunar crystalline \( \text{AuTe}_{1.7} \) compound are formed, thus creating new amorphous-crystal interfaces. Its kinetics, corresponding to the right part of the curves of the fig. 4 follows \( t^\alpha (\alpha < 0.5) \) laws. The \( \text{AuTe}_{1.7} \) compounds is identified by X-ray experiments and electron diffraction microscopy (fig. 7d). Using Au/Te thin film diffusion data (fig. 5), we can explain the curves aspects in respect to the temperature : the nucleation and growth rates of the compound are drastically different : at low temperature \( (80^\circ\text{C}) \) its formation is reduced and the saturation level is typically the gold content of the two first types of short-circuits \( (C \approx 10 \, \text{at.\%}) \), whereas at high temperature \( (120^\circ\text{C}) \) the compound formation is fastest \( (x 50) \), leading to complete interdiffusion \( (C \approx 30 \, \text{at.\%}) \) and reaction (fig. 7d). This compound, used in a barrier configuration, improves the lifetime of the contact by a factor 20 to 100, varying the compound thickness (fig. 6b).
CONCLUSION - Adapted from polycrystalline "defect-enhanced" diffusion model, a three-step diffusion model is proposed to take into account the gold diffusion into the amorphous GeTe₄ thin films. The discussion points out the rough estimations of "gold-capacities" of the inter-globular spaces and the open porosity of the sputtered GeTe₄ material, as well as the oxygen effect.

The model, except for the multiphase diffusion type which is typically due to the low thermal stability of the GeTe₄ material, may describes successfully the metal diffusion behaviour of globular amorphous films.

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