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STABILITY AND ELECTRONIC PROPERTIES OF VACUUM-EVAPORATED AMORPHOUS METALLIC Au-Ge ALLOY FILMS

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Résumé. - On discute les conditions d'existence et la stabilité d'alliages métalliques amorphes Au-Ge préparés par co-évaporation sous ultra-vide. Leurs propriétés optiques sont analysées en contribution de Drude et contribution interbande. On en déduit la présence d'hybridation sp-d dans ces alliages.

Abstract. - The existence and stability of amorphous metallic Au-Ge alloys prepared by co-evaporation under ultra-high vacuum are discussed. Their optical properties are analysed in terms of a Drude and an interband contribution. Occurrence of sp-d hybridization is inferred.

1. Introduction. - Amorphous metallic alloys between a noble metal and Si or Ge have been obtained by different methods (1-5). Their main interest lies in the relative simplicity of the electronic structure of either component. The complex dielectric constant of pure noble metals follows a free-electron behavior up to 2-4 eV, where a strong interband contribution, due essentially to transitions between the filled d-band and the Fermi level, sets in. These properties are little modified in the liquid state (6). Si and Ge are covalent in their solid (crystalline and amorphous) state, due to sp³ hybridization, but metallic in their liquid state, with about four conduction electrons per atom. These alloys are therefore good candidates for testing the validity of a rigid-band model, in which Si or Ge impurities would just add their four valence electrons to the host conduction band. The optical properties of sputtered amorphous Au-Si alloys for Si concentrations between 13 and 50 at.% have recently been interpreted as confirming such a model (7). However, the situation may not be so simple, because of the strong interaction which can be expected between the impurity s-p states and the host d states (8). Moreover, the type of bonding is likely to change, at least locally, when increasing the Si or Ge concentration, which will alter the metallic character of the alloys.

We present here the results of optical measurements on amorphous Au-Ge alloys with Ge concentrations between 20 and 40 at.%. These alloys were prepared by co-evaporation under ultra-high vacuum

in order to avoid spurious effects due to built-in gaseous impurities. Their structure was controlled by electrical resistance measurements and electron microscope investigations. We discuss briefly the existence and stability of amorphous metallic alloys and we analyse their optical properties in relation with different models for their electronic structure

2. Experiment. - The samples are thin (200-400 Å) semi-transparent films deposited by co-evaporation under ultra-high vacuum onto glass substrates maintained at low temperature (15-20 K). The deposit composition and thickness are monitored by two calibrated quartz microbalances. The film reflectance and transmittance are measured in situ just after deposition, between 0.6 and 4.5 eV, with a specially built spectrometer (9). Electrical d.c. resistance measurements performed in situ by a four-probe technique as a function of temperature allow to characterize the as-deposited sample, to determine its stability range and to follow possible structural changes on annealing. Optical measurements are repeated in situ at any desired annealing stage. At room temperature, they are performed both under vacuum and in air with a Cary 14 spectrometer, as a check of the optical data accuracy. The structure of the as-deposited film and its changes upon annealing are traced back from room temperature electron diffraction and electron microscopy results, supplemented by a detailed analysis of the annealing curve. The film thickness is determined by an X-ray interference method (10), its composition by an electron microprobe technique (11).

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3. Existence and stability of amorphous alloys. -

Only the main results are given here. The details of electrical resistance measurements and structure investigations will be reported elsewhere (12).

- For small Ge concentrations (5, 11 at.%) the films always consist in a mixture of pure Au and pure Ge crystallites.

- For Ge concentrations closer to the eutectic, 27 at.% Ge (13) (24, 28, 30 at.%), we obtained amorphous alloys whose structure is characterized by two unsplit broad diffraction rings centred at $s = \sin\theta/\lambda = 0.217$ and $0.380 \text{ \AA}^{-1}$ respectively. This diffraction pattern is very similar to the one reported for a liquid $\text{Au}_{75}\text{Ge}_{25}$ alloy (14) and indicates a simple, close-packed structure with no Ge-Ge bond. These amorphous alloys have initial resistivities between 124 and 138 $\mu\Omega\text{cm}$, with very small negative temperature coefficients: -4 to -7×10^{-5} . Crystallization starts above 250 K with the precipitation of pure Au microcrystallites and, in some cases, the formation of a metastable complex crystalline alloy phase.

- For higher Ge concentrations (34 at.%), we still obtained amorphous alloys, but with a different structure. Their diffraction diagrams present an additional broad ring centred at $s = 0.155 \text{ \AA}^{-1}$ reminiscent of the first diffraction ring of pure amorphous Ge (15). These amorphous alloys have slightly higher resistivities, with more negative temperature coefficients, of the order of -5×10^{-4} . A metastable complex crystalline alloy phase, different from the previous one, appears abruptly just below room temperature.

4. Analysis of optical data. - Measuring both the reflectance R and the transmittance T of a thin film with known thickness allows to determine the complex dielectric constant $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$ accurately at each frequency (16). Unfortunately, in the present case, the computed $\tilde{\epsilon}$ values are extremely sensitive to even very small experimental uncertainties on R and T , which, besides, vary very little with frequency, especially in the near infra-red.

- For Ge compositions between 20 and 30 at.%, the ϵ_1 and ϵ_2 curves for the as-deposited amorphous alloys are significantly different from those for pure Au (figure 1). A metallic behavior is still observed at low energies but the optical absorption is considerably enhanced; an absorption edge

Figure 1. - Optical absorption ϵ_2/λ for a $\text{Au}_{70}\text{Ge}_{30}$ alloy: amorphous (a) and partially crystallized (b), and for pure Au (c).

reminiscent of the onset of interband transitions in pure Au is difficult to detect at higher energies (such an edge shows up immediately when pure Au crystallites appear on annealing, as shown by curve (b) in figure 1).

We tentatively analysed the low energy data in terms of a Drude model which, even in a disordered system, should represent a first approximation to the optical properties associated with conduction electrons:

$$\tilde{\epsilon} = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau_o)} + \epsilon_1^c$$

where $\omega_p = (4\pi N_{\text{eff}} e^2 / m_o)^{1/2}$ (N_{eff} the effective number of electrons per unit volume and m_o the optical effective mass) is the plasma frequency and τ_o the optical relaxation time of the conduction electrons; the constant real term ϵ_1^c accounts for interband transitions occurring at higher energies. Computer-fitting procedures on (ϵ_1, ϵ_2) or directly on (R, T) , as well as graphical methods, were used to determine ω_p , τ_o and ϵ_1^c . Reasonable agreement with a simple Drude model was found from 0.6 up to 2.5 eV. Allowing the relaxation time to be frequency-dependent did not improve the fit significantly. We found for $x_{\text{Ge}} = 30$ at.% (with $\epsilon_1^c \sim 2.5$): $\hbar\omega_p = 14.20$ eV; $\hbar/\tau_o = 2.85$ eV.

Above 2.5 eV, there is an additional contribution to the optical absorption which can be attributed to interband transitions (figure 2). It is much smaller than in pure Au and presents a very smooth edge, which makes any onset energy very difficult to determine.

Figure 2. - Decomposition of ϵ_2/λ for an amorphous $\text{Au}_{70}\text{Ge}_{30}$ alloy (a) into a Drude term (b) and an interband term (c).

- For larger Ge concentrations, the optical spectra corresponding to the as-deposited amorphous alloys are completely different from the previous ones (figure 3). There is a strong absorption maximum in the visible, centred at about 2.4 eV, and no metallic behavior can be detected over the investigated spectral range. Little change is observed through crystallization.

Figure 3. - Optical absorption ϵ_2/λ for a $\text{Au}_{66}\text{Ge}_{34}$ alloy: amorphous (a) and partially crystallized into a complex crystalline phase (γ -AuGe) (b).

5. Discussion. - By co-evaporation under ultra-high vacuum, amorphous metallic Au-Ge alloys could be obtained over a small composition range only and their stability was very limited. For higher Ge contents, although the films were still amorphous, local changes in bonding, perhaps favoured by composition fluctuations, modified the electronic properties of the alloys; optically they were no more

metallic. Different results were obtained on sputtered amorphous Au-Si alloys which, in spite of a structure change above 40 at.% Si (5), had a metallic optical behavior up to 50 at.% Si (7).

The optical properties of the amorphous metallic Au-Ge alloys are nevertheless very similar to those of amorphous (7) and liquid (17) metallic Au-Si alloys. All data follow a Drude law in the near infra-red, with comparable values of the parameters characterizing the conduction electrons behavior. Extremely short relaxation times τ_0 are deduced, about an order of magnitude smaller than in pure liquid noble metals (6) but of the same order of magnitude as in pure liquid Ge (18). The effective number of conduction electrons which can be deduced from ω_p , assuming that the optical mass is equal to the free-electron mass, is quite high: about 2.5 electron per atom on average for $x_{\text{Ge}} = 30$ at.% if we take the same atomic density as in pure Au (19). This value is much larger than the one computed in a rigid band model, about 1.9. In all cases, there is an additional contribution to the optical absorption at energies where interband transitions from the d band occur in pure Au, but it is considerably smoothed out.

All these results suggest that a simple rigid band model cannot be applied, and that the Au conduction band and d band are significantly altered when alloying with Ge (Si). It has been shown theoretically (8) that the electronic structure of a Si impurity in a Cu matrix is deeply modified by sp-d hybridization. This theory explains the characteristic anti-resonant structure observed in the p-partial density of states around Si atoms in dilute Cu-Si alloys by soft X-ray emission (20). A conduction band being far from free-electron-like is therefore expected in the alloys. This conclusion, which was also inferred from magnetic susceptibility measurements on liquid $\text{Au}_{81}\text{Si}_{19}$ alloy (21), is more compatible with the values of the parameters characterizing the conduction electron behavior deduced from the optical data. The sp-d hybridization is also likely to modify the d-partial density of states. A shift of the upper peak of the Au d band towards lower energies, accompanied by a smoothing of the upper edge, has been observed for evaporated amorphous Au-Ge alloys (20 and 40 at.% Ge) by photoemission (3). Such an effect would explain, better than disorder alone, the experimental reduction of the interband

absorption.

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