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PERCOLATION AND SUPERCONDUCTIVITY IN ION-IMPLANTED ALUMINIUM FILMS (*)

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Résumé. — L'implantation ionique de Si et Ge dans des films minces d'aluminium à 8 K conduit à des alliages dont la température critique supraconductrice est fortement augmentée (jusqu'à 8,35 K pour $\text{Al}_{60}\text{Si}_{40}$), et qui présentent une transition métal-non métal pour une concentration en volume de 45 % Si. Ces résultats sont comparés à ceux obtenus par ailleurs pour des films préparés par évaporation à froid.

Abstract. — Ion implantation of Si and Ge in Al thin films at 8 K produces alloys exhibiting enhanced superconducting transition temperatures (up to 8.35 K for $\text{Al}_{60}\text{Si}_{40}$) and a metal-non metal transition at a volume concentration of 45 % Si. These results are compared to those obtained by other authors on films prepared by evaporation on cold substrate.

The electrical conductivity of thin films has recently received renewed attention [1], largely because of its relation to percolation and phase transition problems. Most of the existing information is based on studies of samples prepared by *splat-cooling* from the melt [2], by sputtering [3], or by coevaporation on cold substrates [4]-[6]. Such samples are generally unstable alloys of a metal and semi-conductor or oxide, and the interpretation of experimental results depends rather critically on assumptions concerning their microscopic structure. Specifically, a granular structure (small metallic grains separated by semiconducting or insulating barriers) has been invoked to account for spectacular increases in the superconducting transition temperature T_c of several such alloys [2], [5], [6] : Josephson tunnelling was suggested to

account for overall superconductivity [5], [7], and excitonic [8] or surface plasmon [9] effects were suggested to account for T_c enhancements. In this Letter, we report results from a different approach to the problem. Ion implantation at liquid helium temperatures allows us to introduce chosen impurities into thin films at reasonably uniform — and large — concentrations. Since the implantation is carried out at rather high energies and at temperatures such that no radiation damage annealing takes place, disordering occurs as a result of collisions of the implanted ion with host atoms. We have compared resistivity and superconductivity results on such systems with those obtained from films with nominally similar compositions, prepared by more *classical* methods. We find a metal-non metal (MNM) transition for Al-Ge and Al-Si films at a critical volume concentration of 50 %; superconductivity in both systems, with the maximum in T_c at an Al concentration of ~ 60 vol. %; a definite correlation between the composition dependence of T_c and of the normal

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resistivity. These results are strikingly similar to those obtained for *granular* films [5], except that we find significantly higher maximum superconducting transition temperatures. Our results are discussed in terms of percolation properties, and lead us to suggest that the nature of the disorder in implanted films be examined in detail.

Our low-temperature ion implantation system [10] was briefly described previously [11]. Basically, it consists of a liquid helium post-accelerating lens adapted to the Orsay ion implanter. Under standard conditions, implantation temperatures of ~ 8 K are obtained, and resistivity measurements may be carried out automatically after each implantation at temperatures ranging from 1.5 K to 350 K, using a four-point probe technique. The films (typically 10×0.3 mm², thickness 500-600 Å for Al and 1 000-1 500 Å for Ge) were evaporated on crystalline quartz substrates. The Al film resistivity ratio ρ (300 K)/ ρ (4.2 K) was 3.5-4.0. Size and impurity effects were normalized out by simultaneously measuring the resistivity of the implanted sample and that of an identical film (on the same substrate) shielded from the ion beam. The upper limit of our resistivity-measuring device was 2 000 $\Omega \cdot \text{cm}$, unfortunately preventing a detailed study of the MNM transition.

The measured resistivity is of course a sample average, while the impurity and damage depth distributions [12] are approximately Gaussian for a single implantation energy. In order to improve sample uniformity, implantations were performed at two different energies for Si (30 and 15 keV) and Ge (50 and 25 keV) in Al, and for Al (100 and 40 keV) in Ge. For a given sample, the evolution of the normal resistivity or of T_c was found to depend only on the implanted ion concentration, and not on the sequence of implantations (as long as the sample doping was reasonably uniform). Thus, implantation through a previously implanted layer had no visible effect: this is in contrast to results on Al-H [11], and it indicated that our samples are indeed disordered.

The dose-dependence of T_c and of the normal resistivity at 10 K (ρ_N) for the Al-Si implanted alloy is presented in figure 1. Similar results are obtained for the Al-Ge system. In order to convert the dose-dependence to the alloy composition-dependence also shown in figure 1, three phenomena must be properly accounted for: (i) sputtering [13] of the implanted film by the incoming beam; (ii) recoil-implantation of surface impurities, i.e., oxygen from the surface oxide layer or light impurities cold-trapped on the sample surface (under our implantation conditions, the latter produces ~ 4 atomic layers per hour, and the implantation lasts several hours); and (iii) the possibly high impurity (mainly oxygen) content of the film before implantation. We have assumed that Al sputtering by Si is identical to that of Al by Al (~ 0.3 at/at) [13] and may be neglected. The light impurity-content due to recoil implantation

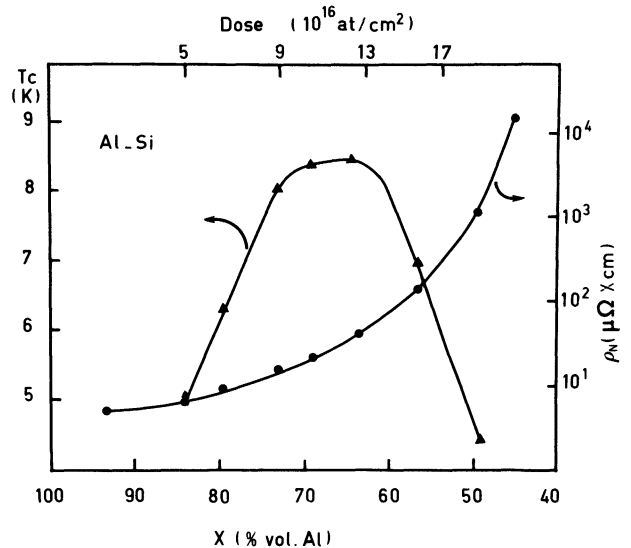


FIG. 1. — Dose and composition dependence of the superconducting transition temperature T_c and of the normal resistivity ρ_N measured at 10 K for a Si-implanted Al film.

was calculated [14] to be < 5 at % at the highest Si implanted dose. Rutherford backscattering (RBS) measurements, carried out with a 1.8 MeV ⁴He beam and a previously described setup [15], revealed that the oxygen impurity content of Al films evaporated on carbon substrates was negligible before and after Al or Si implantation. The situation was more complicated for the Al-Ge system because of the high sputtering ratios of Ge and Al by Ge, and because of the rather large recoil implantation probability. RBS experiments on Al and Ge films [16] before and after implantation at varying doses allowed sputtering ratio evaluations from the residual Al and Ge content of the films. (Typically, the measured sputtering ratio was ~ 7 at/at for Ge on pure Ge, ~ 1 at/at for Al by Ge in $\text{Al}_{0.60}\text{Ge}_{0.40}$ and ~ 0.1 at/at for Ge by Al at the same composition). These experiments also provided quantitative data on the rather large recoil-implantation effects due to the Ge ion beam. Within the uncertainties due to these evaluations, the composition-dependence of ρ_N and T_c for Al-Si and Al-Ge were identical. Note that the pertinent parameter in these experiments is not the atomic ratio, but the metal-to-non metal volume ratio x . Thus, when the Al volume ratio is 60 % in Al-Ge, the volume concentrations of Ge and O are estimated to be respectively (30 ± 3) % and (10 ± 3) %.

For both Al-Si and Al-Ge, the change in the temperature coefficient of the resistivity — i.e., the transition from *semiconducting* to *metallic* conductivity occurs when $x \simeq 0.45$ and the normal resistivity at 10 K is $\sim 10^4 \mu\Omega \cdot \text{cm}$; the resistivity then decreases sharply when $x \simeq 0.50$ (T_c corresponding increases); the maximum T_c -values are obtained when $x \simeq 0.60$ and $\rho_N \simeq 100 \mu\Omega \cdot \text{cm}$. Thus, the highest superconducting temperatures are obtained at extremely high damage levels (typically each atom in the

Al-Si alloy with $T_c = 8.35$ K has been displaced ~ 100 times on average). The influence of disorder is emphasized by experiments [17] in which the samples were annealed after low-temperature implantation (thus inducing segregation), and subsequently reimplanted at low temperature : in all cases, disordering was required to maximize T_c , and our highest T_c values (respectively 7.35 K and 8.35 K for Al-Ge and Al-Si) are much higher than those obtained in granular films (6.6 K [6] and 5.5 K [2] respectively).

The similarity of the composition dependence of T_c and ρ_N in our implanted films (Fig. 1) and in granular structures [1], [5] over the composition range $0.5 < x \leq 1.00$ strongly suggests that a common interpretation of these results be searched for. In both cases, the semiconducting behaviour observed at $0.45 < x < 0.5$ is probably due to tunnelling between Al clusters, with a localization threshold [18] at $x \sim 0.45$. The transition at $x \sim 0.5$ may be discussed in terms of percolation conduction [19].

For three-dimensional systems, the theoretically predicted [19] percolation threshold is $x_c \sim 0.3$, far below the value ($x_c \sim 0.5$) observed in our implanted systems as well as in granular metals [1] whether or not the latter are annealed. It has been suggested [19] that x_c (just as T_c in phase transition studies) may not be a universal quantity, and could depend on the properties of the metal and the non-metal involved. In view of the variety of systems for which $x_c \sim 0.5$, however, other possibilities should be examined. For example, we note that $x_c = 0.5$ is the expected

critical composition for a two-dimensional system. Since the experiments are performed on thin films (their thickness being some 10^5 times smaller than their planar dimensions), their percolation threshold may lie somewhere between the two- and three-dimensional limits [20], as was previously found [21] in the case of phase transitions. Unfortunately, strong variations in the value of x_c are only expected for very thin films, whose thickness is of the order of the metallic cluster size (typically 50 Å in granular films), far smaller than that of our films. The problem clearly warrant further study.

Granular films display a percolation structure [1] on a quasi-macroscopic scale (with rather large clusters). The percolation structure of implanted films is much finer : the presence of small grains cannot be excluded, but in view of implantation-induced disorder, their diameter is presumably far smaller (perhaps 10-20 Å). It remains to be seen whether these structural differences may explain why the maximum T_c is enhanced in implanted films without any change in the percolation threshold [22]. Structural studies of implanted films (before and after annealing) are needed to resolve this point. Tunnelling experiments on heavily implanted samples, recently [23] shown to be possible, should also provide insight into the origin of the T_c enhancement.

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