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Superconductivity in ultra-thin CoSi₂ epitaxial films

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Résumé. — Nous présentons les premiers résultats de supraconductivité obtenus sur des films épitaxiés de CoSi₂ ultra-minces. Ces films métalliques, d'épaisseur variant de 600 Å à 50 Å sont obtenus par épitaxie en phase solide sous ultra-vide. Ces films sont *stables* lors de cycles en température de 350 mK jusqu'à la température ambiante et *supraconducteurs* pour des épaisseurs supérieures à 100 Å. Nous présentons des résultats montrant une diminution de la température critique ainsi que des variations du champ magnétique critique pour des épaisseurs décroissantes des films métalliques. De plus, nous observons un plateau intermédiaire dans la courbe de résistivité en fonction de la température pour le film de plus faible épaisseur (i.e. 100 Å). L'origine physique de ces phénomènes est brièvement discutée.

Abstract. — The first results on the superconducting properties of ultra-thin epitaxial CoSi₂ films are reported. The metal films are obtained by solid phase epitaxy under ultra high-vacuum conditions, with thicknesses ranging from 600 Å down to 50 Å. These films are *stable* against temperature cycling from 350 mK up to room temperature and *superconducting* for thicknesses down to 100 Å. Results showing a reduction of the transition temperature and variations of the critical magnetic field with decreasing film thicknesses are presented. Furthermore, for very low film thicknesses (i.e. 100 Å), an intermediate plateau is observed in the resistivity *versus* temperature curve. The physical origin of these phenomena is briefly discussed.

The epitaxial growth of metallic films on silicon is a very promising new technology due to its many applications, i.e. the Semiconductor-Metal-Semiconductor transistor [1] or the Permeable Base Transistor [2]. Thanks to ultra-high vacuum evaporation techniques, it is possible to grow crystalline metallic films of almost constant thickness (down to a few atomic monolayers) on top of silicon substrates. The epitaxial CoSi₂/Si structure is currently the most extensively studied and consequently the best controlled of these systems [3]. These films, characterized by their extreme cleanliness (less than 0.01 % of undesired elements) present almost ideal crystallographic and surface morphology characteristics [4, 5] for CoSi₂ film thicknesses ranging from 200 Å down to 50 Å. Because of these outstanding properties, CoSi₂ films are good candidates for studying superconducting properties in stable ultra-thin metallic films, since bulk cobalt disilicide has already been reported superconducting at 1.22 K [6, 7].

3×10^{15} cm^{-3} phosphorous doped, $\langle 111 \rangle$ oriented, 2 inch Si wafers are used in this work. After a chemical cleaning described in reference [4], the wafers are loaded in a Riber 2300 Molecular Beam Epitaxy (M.B.E.) apparatus (base pressure $\sim 2 \times 10^{-10}$ torr). The cleanliness of

the Si surfaces is achieved by an *in situ* progressive 900 °C thermal annealing and checked by *in situ* LEED and Auger spectroscopy facilities. Cobalt is electron-beam evaporated (pressure : 10^{-7} torr) with the sample kept at room temperature. The deposited films are then annealed at 650 °C yielding $CoSi_2$ film thickness ranging from 50 Å up to 600 Å. The film thickness is determined at $\pm 10 \%$ by a quartz microbalance previously calibrated by Rutherford Back Scattering spectroscopy on test samples. The bulk $CoSi_2$ lattice mismatch with silicon is 1.4 % so that *strained* $CoSi_2$ films of excellent crystallinity and uniformity are obtained for thickness up to 200 Å; the relaxation of strains then rapidly degrades the silicide film quality from 200 Å to 600 Å [4, 5]. Four-terminal measurements are made at room temperature, yielding the absolute room temperature resistivity, while 4 silver paste contacts are used for low temperature measurements. The samples are attached to the He^3 pot of a circulating He^3 refrigerator. Resistances are measured with a Barras type resistance bridge using a measuring current of 0.8 μA. The bridge resolution at this current level is 10^{-4} Ω, corresponding to a resolution of roughly 10^{-4} μΩ.cm in resistivity. Temperatures are measured with a germanium thermometer whose calibration is checked *in situ* against a He^3 vapour pressure thermometer. « Zero » field critical temperatures are measured in a residual field of 3 gauss, and critical field values are obtained from an average for both magnetic field directions.

First, the resistivity *versus* temperature curves of all samples are recorded from room temperature down to 10 K. The $\rho(T)$ curves show the expected behaviour for the resistivity of a normal metal, i.e., decrease with decreasing temperature and tend towards a residual resistivity ρ_0 at low temperature i.e. $T \sim 10$ K. The residual resistivity ρ_0 is ~ 2.5 μΩ.cm independent of sample thicknesses down to 200 Å and then increases for decreasing film thicknesses (see Table I). A mean free path l is deduced from the residual resistivity data using the free electron model, as listed in table I.

Figure 1 shows the resistivity *versus* temperature curves obtained for the $CoSi_2$ films of thicknesses 100, 200 and 600 Å from 1.2 K down to 0.75 K. Clearly, the three films become superconducting, i.e. the resistivity of the metal films drops rapidly to zero within experimental limits. Contrarily to previous papers focused on localization effects [8], the critical temperature T_c is taken at the midpoint in the resistivity *versus* temperature $\rho(T)$ curve, and the transition width ΔT_c is defined as the temperature interval between the 75 % and the 25 % points in the $\rho(T)$ curves. It is clearly seen in figure 1 that the critical temperature T_c and the transition width ΔT_c decrease with decreasing film thickness. Moreover, an intermediate plateau in the $\rho(T)$

Table I. — *Experimentally determined parameters for the four films described in the text; d_M is the film thickness, T_c and ΔT_c are the critical temperature and the transition width respectively; finally ρ_0 is the residual resistivity of the layer measured at 10 K, l the corresponding calculated carrier mean free path and $R_\square$ the sheet resistance of the films.*

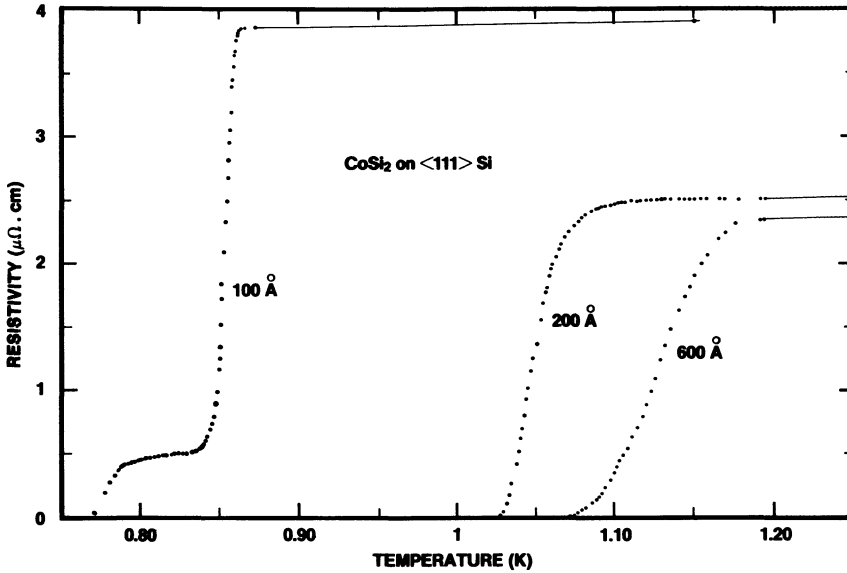| d_M (Å)	T_c (K)	ΔT_c (mK)	ρ_0 (μΩ.cm)	l (Å)	$R_\square$ ($\Omega_\square$)
600	1.121	60	2.3	450	0.39
200	1.047	30	2.5	415	1.25
100	0.852 0.780	13 14	3.9	265	3.9
50	?	?	6.4	162	12.8

Fig. 1. — Resistivity *versus* temperature curves in CoSi$_2$ epitaxial layers for three different thicknesses.

curve is observed for the 100 Å thick film. The film resistivity then drops to zero below a second critical temperature T'_c. Let us finally point out that no variation in the resistivity is observed for the 50 Å thick CoSi$_2$ film from 4.2 K down to 350 mK. Measurements are in progress at lower temperatures. These results are summarized in table I.

The quenching of superconductivity by a magnetic field applied normally to the CoSi$_2$ film is then studied as a function of temperature. The critical magnetic field H_c is defined as an abrupt change in the resistivity *versus* magnetic field curve, recorded at stabilized temperature. Although the experimental data do not allow the determination of the type of superconductivity of these CoSi$_2$ films, the critical magnetic fields obtained are conventionally denoted H_{c_2}, the nucleation field at surfaces (since these experiments are carried out with field normal to thin films) [9]. Figure 2 then shows the H_{c_2} *versus* temperature curves obtained for the three samples. It is to be noted that the $H_{c_2}(T)$ curves for the 100 Å thick sample are shown for the 2 transitions, i.e. for the two critical temperatures T_c and T'_c. For the 100 and 200 Å thick samples, the $H_{c_2}(T)$ curves are parallel, i.e. the slopes are not dependent on the film thickness, while this slope decreases for the 600 Å thick sample. In the investigated temperature range, e.g. $T \sim 0.5$ K, H_{c_2} is clearly in the 100-200 gauss range. We can then roughly estimate a lower bound of the coherence length using $\xi^2 \sim \phi_0/2\,\pi H_{c_2}$, where $\phi_0 = hc/2\,e$ is the flux quantum [9]. Thus, the ξ values are greater than 1 300 Å, i.e. large compared to the film thickness.

Our residual resistivity data are very close to those obtained by J. C. Hensel *et al.* on similar epitaxial CoSi$_2$ thin films [10, 11]. These authors have shown, using the Fuchs transport theory [12], that the surface scattering in these films is essentially (but not purely) specular i.e. little loss of phase coherence is experienced by the carriers during their reflection on surfaces. In this theory, the increase in residual resistivity in the thinner 100 and 50 Å thick samples is accounted for by the diffuse surface scattering component which, although weak and independent on film thickness, acts more strongly on the thinner films. Hence it seems reasonable to think that the inherent bulk resistivity and consequently the bulk critical temperature T_c, which may depend strongly on ρ_0 is independent on film thickness [13, 14].
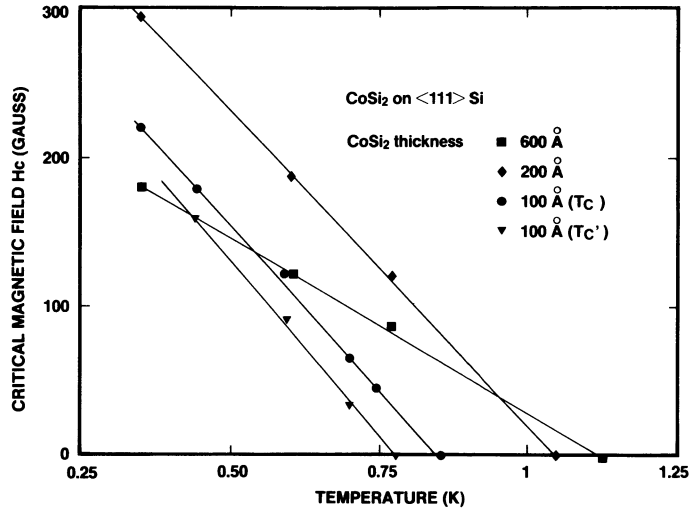
Fig. 2. — Critical magnetic field H_{c_2} *versus* temperature for the three $CoSi_2$ metallic films.

An important point to be noted is that, as listed in table I, the surface resistances $R_\square$ of our films are much below the localization threshold $R_{\square 1} \sim \hbar/e^2 \sim 4\,000\,\Omega_\square$ [15]. This is not surprising since the $CoSi_2$ films are crystalline (epitaxially grown) and are clearly not disordered systems. The observed reduction in T_c is related to localization or fluctuation effects. However, in view of the above remark concerning $R_\square$, these effects are expected to be small in our films and thus unable to explain the magnitude of the observed variations of T_c.

We may think of strain effects as a possible origin of this T_c lowering. Indeed, the thin $CoSi_2$ layers are stretched to match the silicon lattice, so that as the film thickness is increased, the strain stored in the layer increases and the system relaxes. It does so by generating dislocations in the Si bulk [3, 5] and tearing the $CoSi_2$ film apart [4], thus decreasing the strain, but keeping the film still electrically continuous. The pressure dependence of T_c through the Debye temperature θ_D and the density of states at the Fermi level has already been described in bulk metals [18]. The order of magnitude of this dependence could possibly explain the observed variations for the 3 thicker films, with T_c converging towards its reported bulk value for the low-strain 600 Å thick sample. However, this cannot account for the very sharp decrease in T_c between the 100 and 50 Å sample (if this film ever show a superconducting transition at $T < 0.35$ K) as it has been shown that both 100 and 50 Å thick films are similarly stretched [4, 5] and thus experience roughly equal negative pressure.

One may speculate that surface related or two-dimensional effects play a major rôle in the decrease of T_c with film thickness; for instance, the diffuse surface scattering mechanism which plays a minor rôle in the 600 and 200 Å thick films and takes a more active part in the two thinner films may be of importance in the comprehension of the phenomenon. Studies are in progress for a better understanding of the problems involved here.

As far as the plateau in the $\rho(T)$ *versus* temperature curve of the 100 Å film is concerned, this effect could be related to the growing influence of surface roughness. Indeed, such plateaus have already been reported in granular films and two dimensional arrays of Josephson junctions, and have been interpreted as superconducting regions weakly coupled through normal regions [19]. This could apply to our system if we assume that, for thin enough samples, fluctuations in the layer thickness define superconductive $CoSi_2$ islands separated by thinner (and consequently in the normal state at the measuring temperature) metal patches.

In conclusion, we have shown that CoSi$_2$ films epitaxially grown on top of Si substrates are superconducting for film thickness down to 100 Å. Variations in critical temperature T_c, transition width ΔT_c and critical magnetic field H_{c_2} are revealed. The origin of the decrease in T_c with decreasing film thickness is discussed, noting that the low $R_\square$ of our films seems to exclude any localization effects.

Acknowledgments.

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