PHYSICAL REVIEW B VOLUME 43, NUMBER 10 1 APRIL 1991

Superconductivity in ion-beam-mixed layered Au-Si thin films

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(Received 15 October 1990)

The superconducting properties of thin films made by mixing alternating layers of Au and Si using ion-beam bombardment correlate with the formation of metastable metallic phases in what is otherwise a simple eutectic system. Transmission-electron-microscopy measurements reveal the superconducting phases to be amorphous. Compound formation and the nature of Au-Si bonding in these metastable phases are demonstrated from x-ray photoelectron spectroscopy and from a previous study of x-ray-absorption spectroscopy. After mixing with a beam of Xe ions, multilayered films with an average nominal composition Au_xSi_{1-x}, where $x=0.2$, 0.4, 0.5, 0.72, and 0.8, exhibited superconducting transition temperatures in the range 0.2–1.2 K. A double transition feature in the magnetic field dependence of the resistivity is attributed to the formation of more than one metastable metallic phase in the same sample as the ion dose increases.

I. INTRODUCTION

Superconductivity in systems that exhibit a metal-to-insulator transition has been investigated extensively.[1] The effects of localization and electron-electron interactions on the superconducting properties near the transition have attracted special attention. In addition to having a metal-to-insulator transition near $x=0.14$,[2,3] the Au_xSi_{1-x} system is simple to prepare and is of special importance to the electronics industry. Much work has therefore been done on its structural and electronic properties. Gold remains a nonsuperconducting metal down to temperatures in the μK range.[4] Pure Si is semiconducting under ambient pressure but, if subjected to pressure, becomes metallic and at pressures above 12 GPa becomes superconducting.[5–7] However, Au-Si films evaporated from Au-Si alloy ingots onto silicon and glass substrates at room temperature[2,3] and films quenched from the melt onto helium-cooled substrates[8] were found to exhibit superconducting transitions in the composition ranges 18–42 at. % Au and 40–80 at. % Au, respectively.

The equilibrium phase diagram of Au-Si has two liquidus branches characteristic of eutectic-type heterogeneous mixtures. The eutectic temperature is about 370 °C and the eutectic composition is 82.4 at. % Au. No compounds are formed under equilibrium conditions but several metastable metallic phases, both amorphous and crystalline, are obtained by quenching from the liquid or vapor states or by ion-beam irradiation.[8–10] Historically, Au_xSi_{1-x} was the first metallic glass to be synthesized.[11,12]

The Au-Si interface has also been the subject of many studies because of its relevance to device technology. It is important in the present study because of the suggestion in 1964 by Ginzburg of the possibility of synthesizing a high-temperature superconductor by using a Schottky barrier.[13,14] During the evaporation of Au onto clean Si or vice versa, a mixed interfacial region of about 30 Å in thickness forms. Our present work suggests that this layer is mainly made of superconducting material.

Superconductivity in multilayers has attracted much interest in recent years.[15–17] In these studies films of alternate layers of *S*-NM or *S*-SC (where *S* stands for superconductor, NM for normal metal, and SC for semiconductor) were found to exhibit a dimensional crossover from two dimensions to three dimensions as the layer thickness was varied. The *S*-NM systems are considered model systems for studying the proximity effect in superconductors, whereas the *S*-SC systems have been useful for studying Josephson tunneling.

In this paper we discuss the correlation between the superconducting properties and evidence for Au-Si bonding in ion-beam mixed multilayered films of Au-Si. Evidence for compound formation is derived from x-ray photoelectron spectroscopy (XPS) studies and previously published work on x-ray-absorption spectroscopy (XAS).[18] Structural studies using transmission-electron microscopy (TEM) and confirmed by x-ray diffraction indicate that the superconductivity is associated with a metastable amorphous phase.

II. EXPERIMENT

Layered Au_xSi_{1-x} thin films, where $x=0.2$, 0.4, 0.5, 0.72, and 0.8, were sputtered from separate Au and Si sources onto Si or Al_2O_3 substrates in an argon atmosphere. Each film consisted of six layers of Au of equal thickness t_A alternating with six layers of Si of equal thickness t_S. The values of t_A and t_S were chosen so that the total thickness of each film was about 700 Å and so their ratio was in accordance with the desired Au:Si ratio. The thickness of any single layer never exceeded 100 Å.

The samples were bombarded with beams of Xe^{2+}. When impinging on an amorphous target, ions are statistically distributed with a Gaussian peak at an average distance from the surface of R_p (called the projected range) and a standard deviation of ΔR_p (called the straggling). The implantation energies were chosen so that the total thickness of the film was approximately $R_p + \Delta R_p$. Following earlier studies[9] two doses were chosen so as to span a range containing several metastable phases in the "known nonequilibrium" phase diagram of the Au-Si alloy.[10] The doses were 0.5×10^{15} and 5.0×10^{15} ions cm^{-2}. The resistivity was measured in a dilution refrigerator with a minimum temperature of 20 mK and fitted with a superconducting solenoid that was used to produce fields up to 8 T. In the range 300–4.2 K, a liquid-helium-cooled cryostat was used. Rutherford-backscattering spectroscopy (RBS) was used to characterize one of a pair of twin samples immediately after Xe^{2+} implantation. TEM studies were conducted in a 400-keV JEOL 4000FX instrument. Vertical cross-section samples were prepared by bonding two wafers with the film sides face to face using epoxy. These sandwiches were sawn along the desired crystallographic directions, mechanically polished to below 100-μm thickness, and then argon-ion milled with liquid-nitrogen cooling until suitable perforation occurred. The effect of these preparation steps on the structure and chemistry of the samples is not known. XPS was carried out in a Kratos XSAM800 instrument equipped with a multichannel detector, Mg and Al sources, and a monochromator. Binding energies were referenced to the Ag ($3d_{5/2}$) peak at 361.8 eV. The surface layer was Ar-ion milled off at 1 keV before taking the spectra. Data are presented without smoothing or satellite subtraction in order to reduce artifacts. Details of the x-ray-absorption experiment were given in a previous publication.[18]

III. RESULTS AND DISCUSSION

A. Superconducting properties

Our multilayered samples were superconducting even before implantation because of a small amount of mixing at the Au-Si interface, but the superconducting transition temperatures were very low (<0.4 K) and had little (if any) compositional dependence (Fig. 1). Ion-beam mixing was found to increase the transition temperature, as shown in Fig. 2, which compares the resistive transitions in zero magnetic field for samples with the same composition (Au-Si_4) implanted with doses of 0.0, 0.5×10^{15}, and 4.0×10^{15} ions cm^{-2}. T_c was about 0.4 K for the unimplanted film but was enhanced to more than 0.9 K for a dose of 5×10^{14} Xe ions cm^{-2}. When the dose was increased to 4×10^{15} cm^{-2}, T_c fell below 0.3 K and the resistivity curve developed a low-temperature tail characteristic of phase segregation.

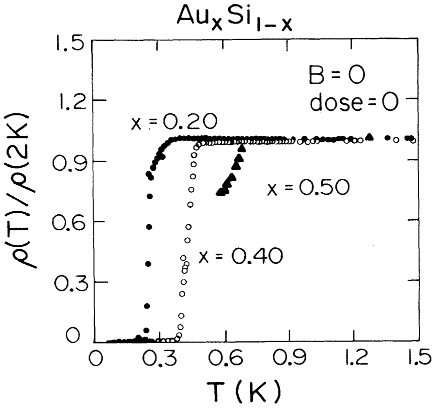

FIG. 1. Resistive transitions of Au_xSi_{1-x} multilayered samples before ion-beam mixing in zero field. The incomplete transition for $x=0.5$ was measured in a helium-3 cryostat with a minimum temperature of 0.45 K.

The sample compositions and thicknesses were checked with RBS using 2-MeV helium ions. Figure 3(a) compares the RBS gold peaks of samples with different values for the gold fraction x implanted with the same dose of 5×10^{14} ions cm^{-2}. These spectra show that the relative stoichiometries of the virgin films are retained. There are features in these spectra which are indicative of the existence of the layers even though these features were not completely resolved at normal incidence. When the spectra were obtained with the helium beam incident at a glancing angle of 75°, as can be seen in Fig. 3(b), the layers were clearly resolved. Both spectra slope upwards at higher channel number because the last layer deposited

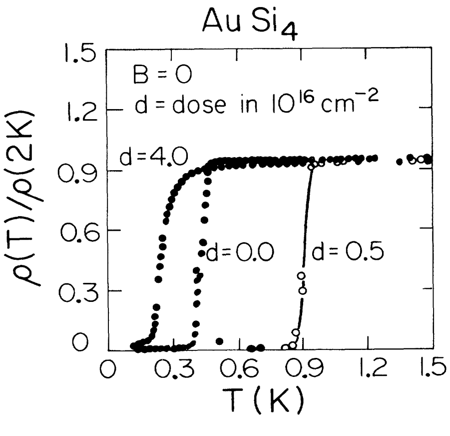

FIG. 2. Resistive transitions in zero magnetic field for samples with the nominal composition Au Si_4 implanted with doses of 0.0×10^{15}, 0.5×10^{15}, and 4.0×10^{15} Xe^{2+} cm^{-2}.

always consisted of Au. This was done to protect the silicon against oxidation. The samples in Fig. 3(a) with stoichiometries around $x=0.5$ have RBS spectra with less structure and less steep slopes. Both these features are signatures of more mixing. These samples had the highest superconducting transition temperatures, as can be seen from Fig. 4(a).

The cross-sectional TEM measurements showed sharp diffraction spots corresponding only to crystalline gold which had either not mixed with silicon during the ion bombardment or precipitated out as the systems began to return to thermodynamic equilibrium. No evidence was found for the metastable crystalline phases reported in the ion-beam-mixing experiments of Tsaur and Mayer.[19] Similarly, the only Bragg peaks found in the x-ray-diffraction measurements were those corresponding to randomly oriented crystallites of gold. The TEM images of the section showed regions of pure gold embedded in an amorphous matrix. The gold regions had the appearance of being unmixed remnants of the original gold layers; but, of course, we cannot rule out memory artifacts of recrystalization.

We suggest that the formation of the superconducting phase and the subsequent enhancement of its superconducting properties occur as follows: Even before ion-beam bombardment, the interface between the Au and Si layers is not exactly sharp. Photoemission spectroscopy studies have indicated a region of about 30 Å in which alloying occurs,[20,21] in spite of the expectation from the equilibrium phase diagram that Au and Si are mutually insoluble. The silicon Auger peak for this mixed region at 92 eV is split into a doublet with peaks at 90 and 95 eV which is taken to be indicative of changes in the local environment and a disruption of short-range order.[22] This interface region is evidently superconducting, but is so thin compared to the neighboring equilibrium Au and Si layers that most of the film is basically normal metallic gold and semiconducting silicon. This causes a lowering of T_c because of the proximity effect of the thick gold layer on the thin superconducting alloy layer. The whole sample can become superconducting only if electron pairs can tunnel through the relatively thick semiconductor and normal metal barriers.

With increasing dose, the mixed (superconducting) layer grows outwards from the interface,[9,19] thus causing increases in T_c and the upper critical field parallel to the

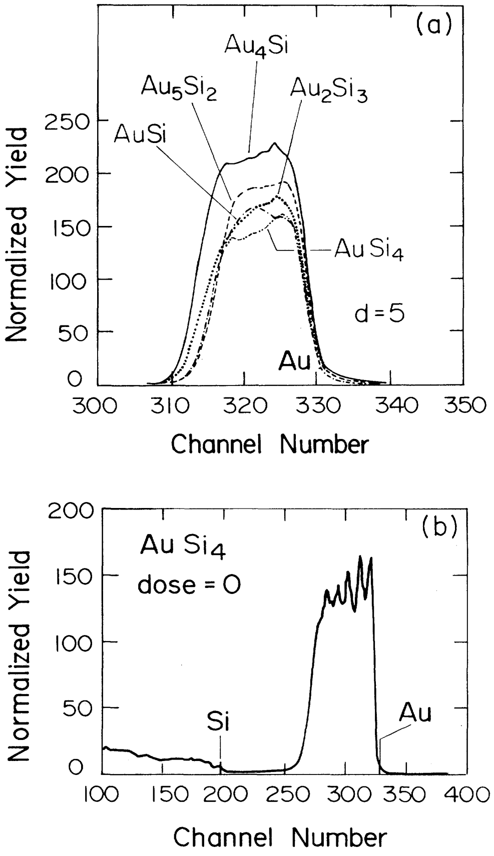

FIG. 3. Rutherford backscattering spectra for multilayered Au-Si samples. (a) Composition dependence of the gold peaks for samples implanted with a dose of 0.5×10^{15} ions cm^{-2}. (b) The gold peak for a AuSi$_4$ virgin film obtained at a glancing angle of 75° revealing the layer structure.

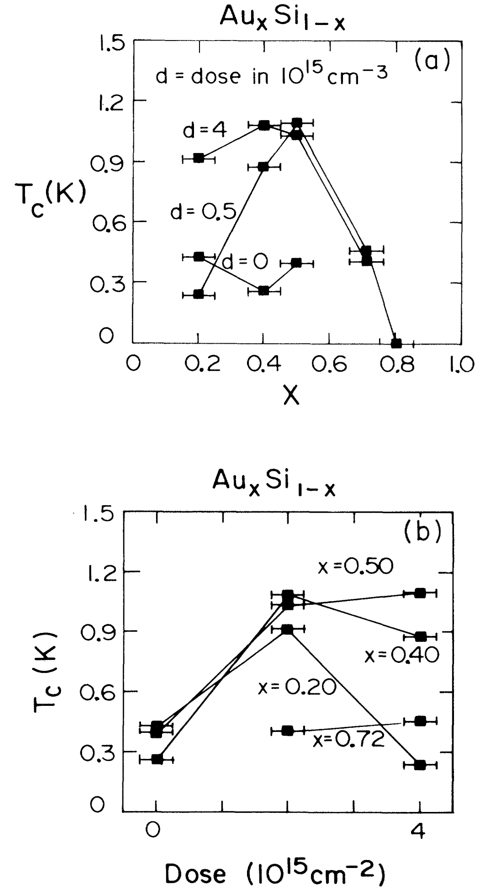

FIG. 4. Variation of the superconducting transition temperature (a) with the nominal composition x and (b) with the implantation dose.

layers, $B_{c2\parallel}$. When mixing is a maximum and the whole film is made up of the superconducting alloy, the superconducting parameters attain their optimal values. Various effects accompanying the implantation process, on the other hand, contribute to the reduction of these parameters, so that T_c versus dose varies in the manner depicted in Fig. 4(b).

Ballistic mixing, radiation damage, and metastable phase formation are some of the processes at play during implantation that are known to affect the superconducting properties. At zero dose there seems to be little dependence of the superconducting parameters on the thickness of the individual layers. This observation is reflected in the dependence of T_c on x as shown in Fig. 4(a). This figure also illustrates that at higher doses T_c assumes a maximum at about $x=0.5$.

We believe that superconductivity is associated with one or more of the metastable metallic phases that are produced during ion beam mixing or interfacial reaction. The double transition in the critical field measurements of Fig. 5(a) suggests that there are two superconducting phases in the ion-bombarded samples. The sample depicted in this figure has the nominal composition Au Si and was given a dose of 4.0×10^{15} ions cm^{-2}. According to the results of Liu *et al.* [9] this dose is sufficient for the production of two metastable crystalline phases and an amorphous phase. Our observations suggest that at this stage of bombardment the sample contains regions with two different but well-defined compositions. Regions near what used to be the Au-Si interface are very well mixed and are made up of a phase with a relatively high $B_{c2\parallel}$. In between are incompletely mixed regions consisting of a lower B_{c2} phase. The zero-field T_c's of the two phases are not different, as evidenced by the sharp single transition of Fig. 5(b). With fields, $B_1 < B < B_2$, where B_1 and B_2 are the values of $B_{c2\parallel}$ fields for phases 1 and 2, respectively, phase 1 becomes normal, thus giving rise to the step in $R\,(B,100\text{ mK})$ of Fig. 5(a). This effect is barely observable when a dose of only 0.5×10^{15} ions cm^{-2} has been given to the sample (Fig. 6). The origin is similar, however, as is supported by the fact that the steps occur at almost identical values of $B_{c2\parallel}$.

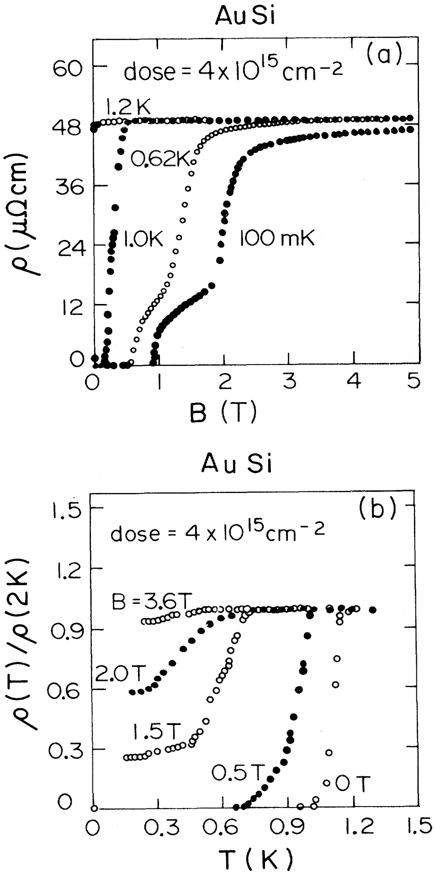

FIG. 5. (a) $\rho(B)$ for $T=0.10$, 0.62, 1.00, and 1.2 K. The figure shows a double transition indicative of the existence of two phases. (b) $\rho(T)/\rho(2K)$ for $B=0$, 0.5, 1.5, 2, and 3.6 T. Note the absence of any double transition in zero field.

The slope of the B-T curve near T_c has been used to calculate $\xi(0)$, the geometric mean of the coherence lengths parallel and perpendicular to the film surface for each phase using

$$B_{c2\parallel}=\frac{\phi_0(1-t)}{2\pi\xi^2(0)}\,, \quad t=T/T_c\ .$$

The sample with the highest dose is the one depicted in Fig. 5(a) with the double transition. The two values for $\xi(0)$ calculated for this sample are 170 and 120 Å, respectively.

B. Au-Si bonding

The inert mixing of Au and Si without chemical interaction between the constituents would not be likely to cause superconductivity. The superconductivity in our film is undoubtedly related to bonding between Au and Si in the metastable metallic phases that are produced as a result of ion-beam irradiation. To test this suggestion we had already carried out an x-ray-absorption study[18] of

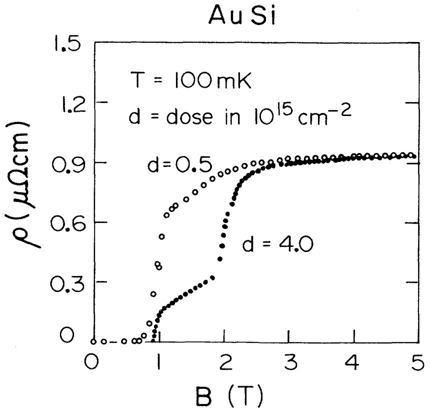

FIG. 6. $\rho(B,100\text{ mK})$ vs B for a sample of AuSi implanted at doses of 0.5×10^{15} and 4.0×10^{15} cm^{-2} showing the evolution of the double transition as dose increases.

films of several compositions and in order to study the nature of the short-range order of the alloy system we have now supplemented that study with x-ray-photoemission measurements. We find evidence for compound formation between gold and silicon from both these studies. For convenience, we show the main results of Ref. 18 in Fig. 7, which compares the near-edge L_3 spectra of multilayered Au-Si films of different compositions and doses with the spectrum of a gold standard. Also shown is the spectrum of an unmixed phase-segregated film. The threshold for transition from the L_3 band to states just above the Fermi level in the mixed films gives rise to the structure known as the white-line (WL) feature. The area of the WL feature is proportional to the number of 5*d* band holes. An estimate of the number of holes per atom created gives about[18] 0.5, which is lower than the value of 0.8 predicted by comparison with studies of equilibrium silicide-forming binary systems like PtSi and PtGe.[23,24] This difference is attributed to the existence of unmixed silicon. The area increases with the increase of the silicon concentration in $\mathrm{Au}_x\mathrm{Si}_{1-x}$ attaining a maximum near $x=0.5$ which is the same composition at which the maximum T_c occurs. Saturation of the WL area occurs beyond that point, indicating that excess silicon is not bonded. The difference in the fine structure features, labeled g_1 and g_2 in Fig. 7, between the mixed films and elemental Au is additional proof that compound formation occurs showing that Au and Si are chemically bonded on a local level.

Additional evidence for bonding comes from the XPS measurements. In Figs. 8(a) and 8(b) we show the XPS valence band and Au 4*f* core-level spectra, respectively, for two Au-Si mixed films. The valence bands for the mixed films are shifted towards higher binding energies and the 4*f* levels towards lower binding energies when compared with their positions for the elemental Au spectra. An increase in the valence-band yield near the Fermi level is also noticeable, which indicates an increase in the density of states. Emission from the Si 2*p* core level was also measured and was found to shift towards higher binding energies.

The core-level shifts are most sensitive to the net charge transfer associated with bond formation between the Au and Si, whereas the valence-band changes depend also on the hybridization between the valence bands of the two elements. This difference is illustrated by the fact that the shift of the 5*d* feature of the Au valence band is opposite to the shift of the 4*f* levels.

The XPS results lead to the following conclusions: Charge is transferred from Si to Au in the metastable compounds. In addition, by hybridization, the Si states enhance the Au *s* and *p* contributions to the valence-band density of states. The Fermi level is thus moved to lower energies relative to the Au 5*d* contribution to the density of states and hence more Au 5*d* holes are created above the Fermi level.

The XPS results also rule out the former suggestion

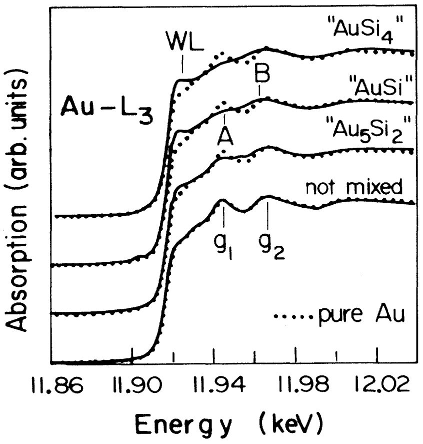

FIG. 7. Gold near-edge L_3 absorption spectra for selected Au-Si ion-beam-mixed films (solid lines) superimposed on elemental Au spectrum (dots). Also shown for comparison is the spectrum for an unmixed Au-Si film. WL is the white-line feature resulting from $2p \rightarrow 5d$ transition, and g_1, g_2, *A*, and *B* are fine structure interference features (from Ref. 18).

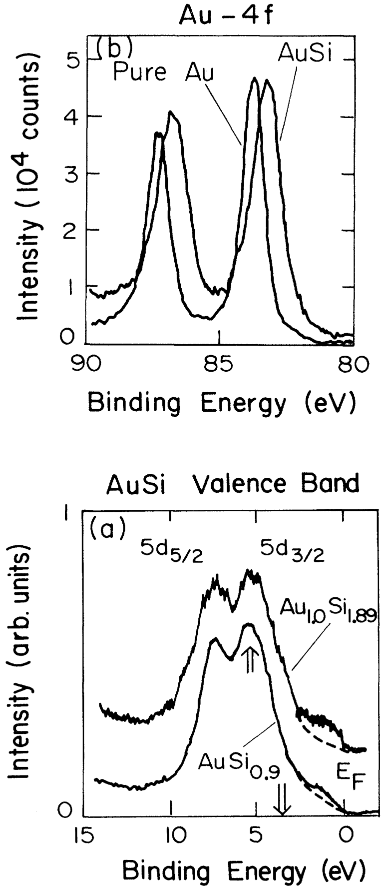

FIG. 8. X-ray photoelectron spectra of ion-beam-mixed Au-Si thin films. (a) The valence-band spectra for two Au-Si films. The arrows indicate the shift in the positions of the $5d_{3/2}$ valence-band peak relative to elemental gold. (b) Au-4*f* core-level spectra for AuSi and elemental Au.

that superconductivity in the Au-Si system originates from a stabilization by the addition of the Au of a higher-coordination liquid state of silicon which is metallic and is similar to the metallic phases formed in silicon under pressure.[6,25,26] The shift of the Si 2*p* core levels is not large enough to account for the required increase of coordination.

C. Mechanisms of superconductivity

Several suggestions have been made to explain the origin of superconductivity in Au-Si.[13,25,27] We have already referred to the proposal of a metallic phase in silicon stabilized by the addition of Au,[25,26] i.e., of chemically simulated pressure. Nonphonon mechanisms like the excitonic mechanism have also been suggested in the case of interface superconductivity,[13,14] and plasmons were claimed to mediate the interaction responsible for superconductivity in the granularlike systems of irradiated Al-Si and Al-Ge.[28] The viability of an exciton-mediated interaction arising at the Au-Si interface is weakened in the present case because of the lack of sharpness in the interface required by the model of Allender *et al.* [13] On the other hand, Nishida *et al.* have suggested the formation of a gold impurity band in the semiconducting silicon gap.[2,27] The electrons in this new band are thought to form a degenerate electron system that presumably becomes superconducting. There is not enough evidence to prove that it is necessary to invoke a nonphononic mechanism in order to account for the observed T_c's; it is possible for superconductivity to arise from the usual electron-phonon interaction in connection with the formation of the metastable metallic phases discussed above. Our results consistently indicate the enhancement of T_c under the conditions that favor the production of the metastable metallic phases and its degradation under conditions of phase segregation.[9] The TEM measurements reported here were not carried out until over a year after the multilayers were mixed by ion-beam bombardment; further relaxation may occur during dicing and sample thinning. This may well explain why there was no evidence from those measurements of the metastable crystalline phases reported by Tsaur and Mayer.[19] The fact that there was little change in the superconducting properties of the samples over this time scale suggests that the crystalline phases are not essential for the superconductivity, unless all the relaxation is occurring during TEM sample preparation.

In summary, we have prepared metastable metallic phases of Au-Si that are superconducting by employing the method of ion-beam mixing. Evidence from XAS and XPS supports the suggestion that compounds are formed and we have found a correlation between the strength of bonding and the superconducting properties.

ACKNOWLEDGMENTS

We thank L. Nazar for help with preliminary TEM measurements, S. S. Laderman for x-ray-diffraction measurements, and N. W. Ashcroft, M. L. Cohen, and M. C. Croft for useful discussions of the interpretation of the results. This work was supported by NSF grant No. DMR-85-11982 and equipment grant No. 84-17901 together with matching funds from Rutgers University.

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