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Superconducting fluctuation effects at a silver-germanium interface

Y. Liu, B. Nease, and A. M. Goldman

Center for the Science and Application of Superconductivity and School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455

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Structures consisting of various layers of Ag and Ge were fabricated in ultrahigh vacuum by quench condensation onto substrates held at liquid-helium temperatures. The electrical conductances of these structures measured *in situ* exhibited incomplete superconducting transitions and superconducting fluctuation effects. It is suggested that these may be a consequence of phenomena occurring at a Ag-Ge interface, rather than properties of atomically mixed Ag and Ge.

The metal-semiconductor interface has been the subject of intensive study for more than two decades because of its technological and scientific importance.[1,2] One of the outstanding problems is whether superconductivity is possible as a consequence of effects occurring across an interface. In this regard, a classical theoretical prediction is that the metal-semiconductor interface is the geometry in which one might find excitonic superconductivity.[3]

The interface between Ag and Ge is especially interesting in that neither element by itself is superconducting at atmospheric pressure. Therefore superconductivity, if it were observed in the absence of the formation of alloys or intermetallic compounds, could only be associated with the interface. It is generally believed that superconductivity in the Ag-Ge and related systems, such as the Au-Ge system, is due to compound formation, alloying or the stabilization of an amorphous Ge phase. Both the metastable hcp Ag_4Ge compound[4] and films of Ag_xGe_{1-x} (Refs. 5 and 6) grown on substrates held at liquid-helium temperatures have been reported to be superconducting. For the latter, superconductivity was found over a very narrow range of compositions near $x=0.5$,[5,6] and has been attributed to a metastable "metallic" amorphous phase of Ge stabilized by adding Ag.[7] On the other hand, more recently, superconducting fluctuations have been observed in Ag films grown epitaxially on Ge substrates held at ambient temperature[8] and at 160 K.[9] In these instances the superconductivity was attributed to effects involving the Ag-Ge interface.

In this paper, evidence is presented of superconducting fluctuations in a system of Ag-Ge interfaces prepared by *in situ* deposition in an ultrahigh-vacuum (UHV) environment onto substrates held at liquid-helium temperatures. This technique is a useful approach to the fabrication of interfaces as interdiffusion of the constituents is greatly reduced relative to ambient temperature deposition. Specifically, sandwich structures of the form Ge/Ag/Ge and overlays of Ag by Ge have been found to exhibit superconducting fluctuations. In contrast to what was reported in Ref. 8, single interfaces formed by depositing very thin layers of Ag onto Ge films were not superconducting down to the lowest temperature reached (≈ 0.5 K). The present results are similar to those reported on Ge/Au/Ge structures prepared at room temperature.[10] However, as will be discussed below, the superconductivity of the latter appears related to intermixing of Ge and Au at an atomic level. It will be argued that the observed superconducting fluctuations in the present work may be attributed to effects at an Ag/Ge interface.

Samples used in this study were prepared by vapor deposition using an apparatus in which a molecular-beam growth chamber was combined with a cryostat.[11] The growth chamber had a base pressure below 2×10^{-10} torr, with the principal residual gas being H_2. The low-temperature apparatus, which was equipped with a ^{3}He evaporation refrigerator, was attached to the top of the growth chamber. The sample holder and refrigerator assembly to which it was attached could be lowered into the growth chamber for film deposition and retracted up into the low-temperature apparatus for measurements. The sample was kept at temperatures no higher than 4.2 K between measurements in an environment in which the base pressure was substantially lower than that of the growth chamber. The substrate temperature during depositions was held at temperatures between 15 and 18 K. Under these conditions H_2 gas absorbed on the surface was desorbed. The film thicknesses quoted below are nominal and are derived from readings of a calibrated quartz crystal microbalance which is sensitive to deposited mass per area. The sheet resistances of the samples were measured by a dc four-point probe technique. The *I-V* characteristic were found to be linear.

A bilayer structure of the form Ag(23.7 Å)/Ge(6.0 Å), with Ge as the bottom layer, was grown at low temperatures. Its sheet resistance versus temperature $R(T)$, measured in nominally zero magnetic-field, exhibited no drop in resistance down to the lowest accessible temperature attained in this study (0.5 K). When a 5.4-Å-thick layer of Ge was deposited on top of this structure to form a Ge (5.4 Å)/Ag(23.7 Å)/Ge(6.0 Å) sandwich the resistance at 14 K dropped from 1.715 to 1.287 kΩ. Moreover, $R(T)$, as shown in Fig. 1, changed dramatically. In nominally zero magnetic field, there were noticeable drops in resistance around 5 and 0.8 K. These features were found to disappear when a reasonably high magnetic field (2100 G) was applied. In this field, at low temperatures, the conductance was a logarithmic function of temperature. In zero field there was no logarithm. In the absence of superconducting fluctuations, or a partial superconducting transition, a logarithmic dependence would be expected for a metal film.[12] There is no obvious explanation for the results shown in Fig. 1 other than the occurrence of a par-

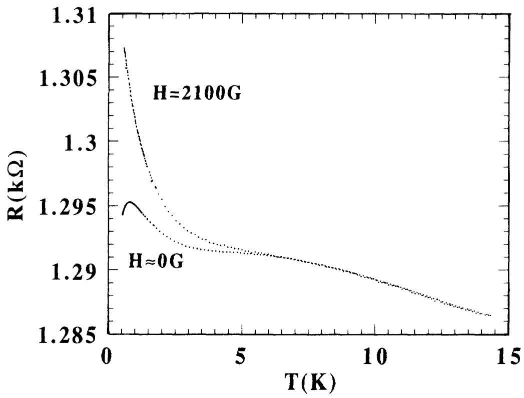

FIG. 1. Normalized resistance $R(T)$ of a Ge(6 Å)/Ag(23.7 Å)/Ge(5.4 Å) sandwich structure measured with and without magnetic field. Here T is temperature, the 6-Å-thick Ge film is the bottom layer, and the applied field was 2100 G.

tial superconducting transition together with its associated fluctuation effects which can be quenched by a magnetic field.

In Fig. 2, the sheet resistance of the Ge/Ag/Ge sandwich described above is plotted at various temperatures as a function of the value of a perpendicularly applied magnetic field H. With decreasing temperature, starting around 5 K, the sample starts to show finite positive magnetoresistance. Furthermore, the magnetoresistance is a linear function of magnetic field, which is also expected for superconductivity fluctuations. All film structures consisting of at least a single Ge/Ag/Ge sandwich exhibited essentially the same behavior, although in some samples (not shown here) the drop at about 5 K was more substantial.[13]

It is important to note that structures consisting of a single film of Ag deposited onto a single Ge film did not exhibit superconducting fluctuations down to the lowest accessible temperature (0.5 K). The "opposite" geometry, Ge films on top of Ag films, was also studied. The conductivities of these bilayers were greatly enhanced relative to that of the original Ag film, and enhanced to a somewhat greater degree than when Ge was deposited onto the Ag layer of an existing Ag/Ge bilayer. An example, shown in Fig. 3, is the case of a 35-Å-thick Ag film, where the addition of 1 Å of Ge resulted in a fourfold increase in conductivity. If there were no intermixing, this result would suggest striking effects at the interface. A significant increase of resistances of films of this type with applied magnetic field was observed, in contrast with the essentially negligible effect of magnetic field on the conductivity of an isolated Ag film. This is strong evidence for superconducting fluctuations, although a superconducting transition or partial transition was not observed down to the lowest available temperature (1 K in this case). Definitive proof of superconductivity would require measurements at substantially lower temperatures.

The question as to whether the apparent superconducting phenomena in Ge/Ag/Ge sandwiches is an interface effect, or a result of mixing or alloying of the elemental constituents is obviously controversial. It can be best addressed by scrutinizing the substantial literature on interfaces of these materials. By doing this one can conclude that there is little atomic level mixing when successive layers are deposited onto substrates held at room temperature. Thus there should be even less when the substrate temperatures during deposition are between 15 and 18 K as in this work.

It should first be noted that Ag and Ge do not mix with each other in bulk at room temperatures since the solid solubility of Ge in Ag, or vice versa, is negligible.[14] Electron-diffraction studies carried out on "amorphous" Ag_xGe_{1-x} films prepared by deposition onto substrates held at low temperatures have revealed the presence of small Ag clusters.[15] This technique does not preclude the possibility of the coexistence of clusters and a mixed Ag/Ge phase at the boundary between the clusters and Ge. On the other hand, low-energy electron diffraction,[16] and photoemission and high-energy electron-diffraction studies,[17] of the growth of Ag on Ge(100) surfaces at room temperature, with one exception,[18] indicate that in this case there is no detectable intermixing or compound formation.

The interdiffusion of Ge deposited onto Ag films to our knowledge has not been studied directly. It is possible that interfaces formed when Ag is deposited onto Ge and

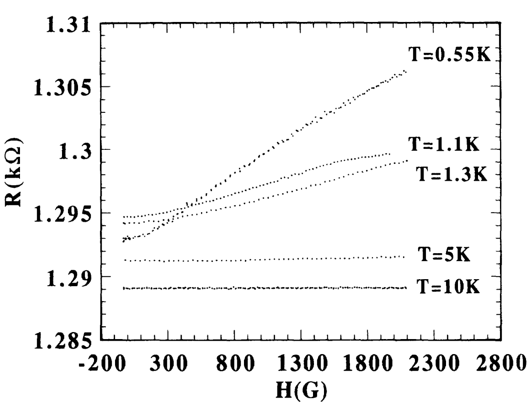

FIG. 2. Resistance of the structure described in Fig. 1 as a function of magnetic field for various temperatures.

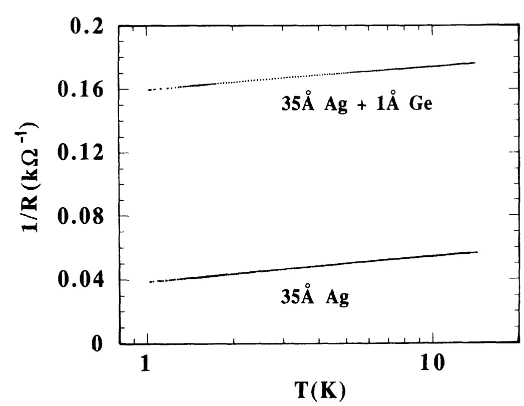

FIG. 3. Variation of the conductance $G = 1/R$ with the logarithm a temperature of a 35-Å-thick Ag film, and the same film overlayed with a 1 Å thickness of Ge.

when Ge is deposited onto Ag are different. On the other hand, the Au-Ge system has been studied. In this instance, as will be discussed below, there is intermixing, however, the degree of interdiffusion is lower for the case of Ge deposited on Au than the other way around.[19] The general discussion of Ref. 19 suggests that for the Ag-Ge system, Ge grown on Ag would be less likely to be intermixed than Ag grown on Ge, which as discussed above, does not mix. Of course, a direct study would be needed to categorically rule out intermixing when Ge is deposited onto Ag.

Interface and percolation effects could explain why Ag layers deposited onto Ge do not exhibit superconductivity, whereas Ge/Ag/Ge sandwiches and Ge layers deposited onto Ag do. A Ag film deposited onto a Ge layer would consist of crystalline clusters which would probably not form a connected network of Ag/Ge interface structures. This situation would probably not change even if the Ag film were made thicker as Ag forms grains when quench deposited, and the bottoms of the grains may not fully cover the Ge surface. On the other hand, in sandwich structures, and for Ge films deposited on top of an already conducting Ag film, a connected network of interfaces would form readily upon deposition of an overlayer of Ge because the latter would form as an unclustered amorphous layer.

An alternative to the interface picture is the idea that the superconductivity could be a consequence of simply the small size of the Ag clusters embedded in Ge. In recent work involving crystalline (not amorphous) Bi clusters embedded in amorphous Ge, the data were interpreted as indicating the small clusters themselves were superconducting, in contrast with the case of crystalline Bi which is itself not a superconductor.[20]

The nominally similar system of Au-Ge is different from the Ag-Ge system in that mixtures prepared by low-temperature evaporation are superconducting over a broad range of compositions and exhibit a range of transition temperatures.[6] In contrast, superconductivity in the Ag-Ge system superconductivity is found only for 50-50 mixtures and at a well-defined temperature.[5,6] Electron diffraction indicates that the Au-Ge system forms an amorphous structure, with Au atoms occupying voids in the Ge network.[15] Insofar as structures prepared at ambient temperatures, such as those studied in Ref. 10, detailed photoemission studies, in contrast with the Ag/Ge results, suggest strong intermixing at Au/Ge interface.[19,21,22] Low-angle x-ray diffraction has shown that for alternating multilayers of Au and Ge, the metastable Au-Ge alloy with the tetragonal structure dominant when layer thicknesses are less than 15 Å.[23] All these studies suggest that superconductivity in the Au-Ge system follows from intermixing at an atomic level.

As we have already pointed out, the superconductivity reported in various Ag-Ge systems has conventionally been attributed to compound formation[4] or Ag-Ge alloying on an atomic scale,[5,6] with the only exception being the work presented in Ref. 8 in which the indications of superconductivity were attributed to effects specific to the interfacial system. As an aside, it is interesting to speculate on the possibility that the superconductivity of the compound Ag_4Ge ($T_c = 0.85$ K),[4] and of the quench condensed $Ag_{0.5}Ge_{0.5}$ mixtures ($T_c \approx 1.2$–1.6 K) (Refs. 5 and 6) are also due to interfacial effects. The "amorphous" Ag_xGe_{1-x} films studied in Ref. 15 were prepared in the same manner as those used in Refs. 5–7. The observation of small Ag clusters in these films suggests that the superconductivity observed in Refs. 5 and 6, in quench-condensed Ag-Ge mixtures is due to interface effects. This hypothesis could explain why Ag-Ge mixtures, in contrast with atomically mixed Au-Ge mixtures, were superconducting only around the composition of 50% of Ag or Ge, and not over a wide range of compositions. In this case the narrow range of compositions for superconductivity could be understood as a consequence of the percolation threshold being very close to 0.5 in two dimensions.[24] Only at threshold would there be a connected path of Ag/Ge interfaces (an "infinite" cluster) spanning the sample to form a connected superconducting path.

The case of the superconductivity of the Ag_4Ge compound is particularly intriguing.[4] This material was prepared using a rapid quenching technique, and the structure was determined using x-ray-diffraction analysis. The superconducting transitions were determined magnetically, and were poorly defined in temperature. No data were presented on the percentage of the diamagnetic phase which would be needed to demonstrate that the superconductivity was a bulk effect. The x-ray-diffraction technique used to identify the Ag_4Ge structure would not be sensitive to crystalline phases present below about 5-at.% level. Thus there is the possibility of the presence of free Ag and Ge in the samples, below the detection limit of the x rays. In this event, the interfacial effects as discussed here could be the origin of the observed diamagnetic response. The nature of the superconductivity of Ag_4Ge should be considered to be an open question which in principle could be answerable using techniques currently available. Correspondingly, it might also be possible, at least in principle, using appropriate techniques, to search for the presence of Ag_4Ge at Ag/Ge interfaces prepared at low temperatures as described here.

In summary, we have observed behaviors in both the temperature and magnetic-field dependence of the resistance indicating partial superconducting transitions and fluctuations in Ge/Ag/Ge structures formed by deposition onto substrates held at low temperatures. Fluctuation effects were also observed in bilayers consisting of Ge deposited onto Ag. The same behaviors were not observed in bilayers formed by depositing Ag films deposited onto Ge, down to the lowest temperatures accessible, 0.5 K. Since various surface and x-ray studies suggest that, in contrast with the Au-Ge system, there is no intermixing of Ag and Ge, the origin of the superconductivity would appear to be associated with the interface effects. There are several possible mechanisms which can lead to the superconductivity at Ag/Ge interfaces. These include excitonic superconductivity, as proposed in Ref. 3, or in the context of conventional theory, the modification of the density of states near the interface. More detailed studies of the conductance, together with investigations of the Hall effect and the tunneling conductance down to lower temperatures than currently available would be required for a more complete elucidation of the behavior at Ag-Ge interfaces and their apparent superconductivity.

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