Insulating phase of mercury in thin quench-condensed films

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(Received 1 November 1994)

We present experimental evidence that mercury forms an insulating phase in films condensed on glass substrates at liquid-helium temperatures. This insulating phase is metastable and it exists in films only up to some critical thickness $d_c \approx 60$ Å. Our results cannot be explained by the assumption that the films consist of isolated islands. We believe that similar insulating phases exist also in quench-condensed lead films and maybe in some other metals. As far as we know the possibility that a disordered system of metallic atoms may form an insulator has never been considered.

A standard way to produce disordered metallic films is vapor deposition at cryogenic temperatures. In most quench-condensed films the onset of the electric conductivity corresponds to a very low film thickness of $d \sim 10$ Å. It is a direct consequence of the low atom mobility. However, there exist a few metals which have no finite conductivity if the film is thinner than 60–80 Å. The first observation of this unusual behavior was reported for mercury films more than fifty years ago.[1,2] These films were deposited on glass substrates at $T=20$ K (the same results were obtained later at liquid-helium temperatures.[3,4] A similar value of d_c has also been observed for the conductivity onset in lead films.[5,6] The usual explanation of the high d_c values is that these films consist of metallic grains with vacuum gaps between them. An increase in the film thickness above d_c closes the gaps between the grains and makes the film electrically continuous. This model was proposed, in one of the first papers[2] on this topic, and it seems to be commonly accepted now.

We want to propose here a different explanation of this phenomenon. We suggest that these metals form insulating amorphous phases when condensed at low temperatures. The most probable explanation is that the low film density is responsible for the insulating behavior. These insulating phases are metastable and an increase in the film thickness causes a transition to a more dense conducting state. The mechanism of the transition should be similar to that observed in some quench-condensed amorphous metals when the film growth leads to a transition to crystalline phases. This transition can be jumpwise[7,8] or continuous[9,10] depending on the film material (see also Ref. 11 and references therein). Some experimental results presented in this paper support our idea.

Films were prepared and studied in a stainless-steel evaporation chamber, which was completely immersed in liquid helium. A substrate and a quartz thickness monitor were placed in the upper part onto a block with a small helium container separated from the main bath. The glass substrate was indium sealed to the opening of the container. The bottom surface of the substrate faced the vacuum of the chamber, while the top one was in contact with helium in the container. We were able to heat the substrate up to the room temperature while the body of the evaporator remained in liquid helium. This baking procedure was used to clean the substrate, taking advantage of cryopumping. The same procedure was carried out as the last one in every experimental run to remove the old mercury film from the substrate.

A mercury droplet was contained in a closed glass capillary in the bottom part of the chamber. A special crash device was used to open the capillary after cooling the chamber down to liquid-helium temperature. The mercury amount was large enough for multiple experiments. A magnetically operated shutter was used to fix the deposition time.

A shadow mask was used to form two identical films. The contact pads were made of platinum deposited by dc sputtering. One of the films was covered by an additional shutter. Thus, only one film was exposed to the mercury beam at the beginning. This shutter could be opened irreversibly by breaking a thin wire lock with a current pulse.

In the first experiment, we used our additional shutter to prepare two films with slightly different thicknesses. The first step was an evaporation of 5 Å of mercury on one of the films. Then the shutter was opened and the following deposition went on at both films simultaneously. The substrate temperature during the deposition was

0163-1829/95/51(8)/5514(4)/$06.00

$T=4.2$ K. The first measurable conductivity (the film resistance $R_{\square}\sim 10^{11}$ Ω) had appeared when the thickness of the first film Hg1 reached the value $d\approx 58$ Å. An additional deposition of 4 Å of mercury decreased the film resistance to $R_{\square}=3\times 10^{8}$ Ω. At that moment the film Hg2 was 1 Å below d_c and we had no conductivity through this film.

Annealing curves for these films are shown in Fig. 1. We carried out the annealing by varying temperature up and down to distinguish irreversible and reversible parts of $R_{\square}(T)$. During the annealing of the film Hg1, we had an extremely steep irreversible decrease of the resistance at very low temperatures: in the temperature range between 8 and 15 K, the film resistance changed by three orders of magnitude [Fig. 1(a)]. In the case of the film Hg2, one can see a drastic decrease in the resistance of the originally nonconducting film [Fig. 1(b)]. This decrease was accompanied with resistance jumps. One of these jumps is shown in the inset. A much larger jump can be seen in this figure at $T\approx 36$ K: the resistance dropped down to 0.1 of its value for the time less than 1 sec (1 sec is a time delay between successive measurements). Resistance jumps were observed only at temperatures $T>20$ K and if the film resistance was large enough.

During another experimental run, we tried to find a thermally activated transition to the conducting state in the film with $d=49$ Å deposited at $T=4.2$ K. Although this film was only 10 Å far from d_c, we did not succeed. The film was heated up to $T=95$ K, but no conductivity appeared. The substrate was cooled down back to $T=4.2$ K after this annealing and we began the second evaporation in order to find the transition to the conducting state. The conductivity appeared on both films simultaneously after the evaporation of an additional 43 Å of mercury. The total thickness for the conductivity onset in this case $d=92$ Å.

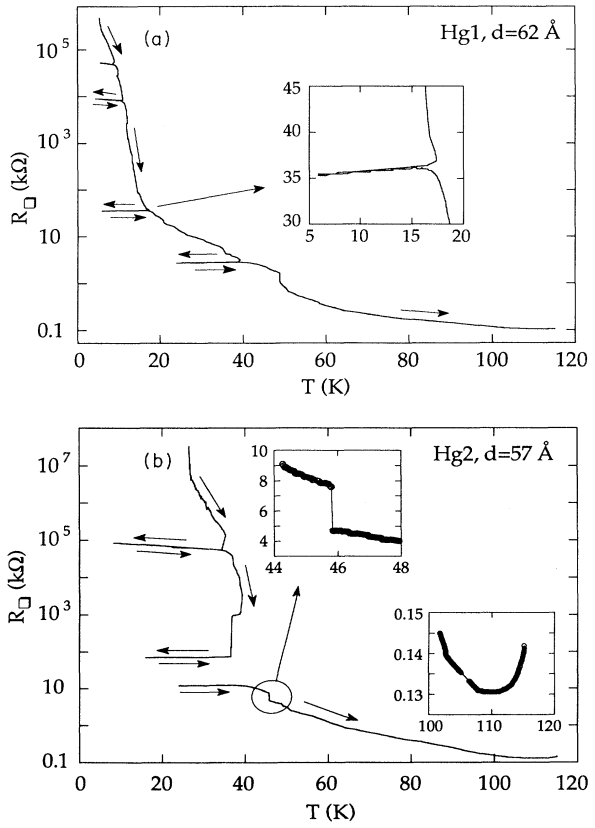

FIG. 1. (a) and (b) Film resistance versus temperature. Insets show details of these dependencies in a linear scale.

If the metastable insulating phase of mercury exists in cold deposited films, an increase in the substrate temperature during the condensation should promote the transition to the conducting state and one can expect a decrease of d_c. This assumption was found to be in complete agreement with the experiment when the substrate temperature was $T=38$ K. In this case, a noticeable conductivity appeared when the film thickness was $d=42$ Å. This value is sufficiently smaller than the critical thickness $d_c=60$ Å for deposition at the liquid-helium temperature. At this temperature, the film was deposited to a total thickness of $d=43$ Å and its resistance $R_{\square}(38\text{ K})=70$ MΩ. Cooling of this film caused growth of its resistance and $R_{\square}(4.2\text{ K})=110$ MΩ.

We have repeated mercury deposition, at $T=4.2$ K, a few times at the beginning and at the end of our series of experiments. The critical thickness $d_c\approx 60$ Å has been found to be the same within a few percent accuracy of our measurements. Moreover, the conductivity onset in two films deposited simultaneously occurred at the same moment with a much better accuracy.

We should note that the phase of deposited mercury is dependent on the substrate properties. The evaporation of mercury on glass substrates as well as on substrates made of single-crystal silicon or germanium leads to the growth of the insulating phase.[3,4] However, one can observe the growth of the conducting phase on the surface of conducting mercury films. This result is not surprising since the interaction between the substrate and incident atoms should be extremely important for the phase formation.

In order to explain the huge irreversible decrease of the film resistance during the annealing in the granular model, one has to expect that a temperature rise forces mercury atoms to move and to close gaps between grains. However, these temperatures (10 K) for the film Hg1 and 35 K for Hg2) are too low to think that the atoms have sufficient mobility along the substrate for this kind of movement. Furthermore, a possible mobility of atoms usually leads to a so-called film melting. It is a process when an originally uniform film divides into small metallic droplets (at low temperatures these droplets are small crystalline particles). This melting temperature for our mercury films was about 110 K. The beginning of the resistance increase corresponding to this process is shown in the inset to Fig. 1(b). Further temperature rise led to the disappearance of the film conductivity.

The second feature which is difficult to explain in the frameworks of the granular model is the resistance jumps during the annealing. We have observed many jumps of different amplitudes in different films. During the largest one, the decrease in the film resistance was about two or-

ders of magnitude.

On the other hand, all the phenomena we have observed can be easily explained by the idea that we are dealing with a metastable insulating phase of mercury. In this model, a sharp decrease of the film resistance during the annealing reflects a thermally activated transition to the conducting state. The transition to the conducting state during the deposition is caused by the kinetic energy of condensing atoms. For this kind of transition, a high atom mobility is not necessary since even small displacements of atoms can lead to sufficient changes of the film structure.

Let us consider the simplest case when a material of our film can be either in some metastable or in the equilibrium state. The metastable estate can be stable during the deposition only if perturbations caused by condensing atoms are not sufficient to overcome the potential barrier ΔU between these two states. An increase of the film thickness reduces this barrier.[12] In disordered films, the barrier height should be different in different regions. Hence, the transition to the equilibrium state can begin only in a few local regions of the film where ΔU is small enough. If the self-heating of the film due to the latent heat of the transition is sufficient to accelerate the transition nearby, it should cause an avalanche process throughout the film. In the opposite case, an increase in the film thickness will lead to a gradual replacement of the metastable state by the equilibrium one. In the case of mercury, we are definitely dealing with the gradual transition.

The film annealing in this model can lead to a thermally activated transition. The probability of the transition in some region i of the film should be proportional to $\exp(-\Delta U_i/T)$. If the temperature rise is slow, these transitions will happen in regions where $\Delta U_i/T > 1$, their frequency must be small, and one has to expect a continuous reduction of the film resistance. In the opposite case of the fast temperature rise, one can reach a situation when many regions with $\Delta U_i/T \sim 1$ exist in the film. A transition in one point can stimulate transitions nearby and cause an avalanche. It is most probable that such avalanches will happen in a limited film area. For example, a part of the film where the transition has already happened can block the avalanche; the avalanche can be blocked also by a region where $\Delta U_i/T \gg 1$. We believe that such limited avalanches are the reason for the resistance jumps during the annealing. The temperature in the avalanche region is not strictly connected to the substrate temperature since a heat release due to the transition is dominant. This heating effect can explain that sometimes resistance jumps have been observed during the decrease of the substrate temperature [Fig. 1(b)].

A transition caused by the deposition should begin near the film surface since the influence of incident atoms is most important there. This transition is to increase the film density due to a momentum of condensing atoms towards the substrate. A somewhat different situation arises during the annealing. In this case, a transition can happen in a limited region inside the film. The only way to increase the film density inside some region is to decrease it outside. This kind of transition should enlarge the density fluctuations across the film. In thin films this process can lead to a film disintegration because almost all the material will concentrate in separate clusters. If the film is thin enough, its disintegration can begin before the transition to the conducting state. We consider this process as an explanation that the film with $d = 49$ Å has shown no conductivity, in spite of the annealing up to $T = 95$ K. The insulating phase of mercury should be formed again in gaps between clusters during the extra deposition. It can explain that we had to deposit an additional 43 Å of mercury to reach the conductivity onset in this experiment.

Let us consider now a possible structure of the insulating phase made of metallic atoms. We start from the model built by numerical simulation.[13] This model was developed to consider the condensation of metallic atoms through a layer of superfluid helium.[10,14] We believe that the main features of the model structure, such as small average density, very high degree of the disorder, and large density fluctuations, on a short-range scale, are similar to that in real mercury films.

In highly disordered films, many different metastable states exist. Therefore, the transition to the conducting state is more complicated than we have considered. The deviation from our simplified model is not of great importance and all of the cases considered above are applicable to this case as well. The transition should be more gradual and one can expect that the conducting phase of mercury obtained at low temperatures is also amorphous.

The superconducting properties of mercury films are also unusual. For example, a global superconducting transition exists in mercury films up to sheet resistance values as high as 10^6 Ω/□.[3] The explanation of this behavior proposed in Ref. 15 is consistent with the existence of the insulating phase of mercury.

It is interesting to note that the main properties of mercury films are very similar to that of bismuth and cadmium films deposited through a layer of superfluid helium.[10,14] This includes high d_c values for the conductivity onset as well as an existence of global superconductivity up to very high values of the sheet resistance. It has been clearly shown experimentally that bismuth forms an insulating phase when deposited through a superfluid helium layer.[10]

This work was supported by the International Science Foundation (Grant No. RID000) and the Swiss National Science Foundation.

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