Thin Films*

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Introduction**MASTER**

In the trivial case, thin films can be used to make very small amounts of a given substance with essentially the same properties as larger samples of the bulk material. The real fascination with the physics and metallurgy of films, however, involves physical phenomena and materials which are unique to films. In this very brief survey we intend to discuss some of the more interesting special properties of films, and mention a few of their important technological applications.

Preparation

Films can be prepared in a variety of ways. A traditional way is by electroplating onto metallic substrates. More recent techniques involve evaporation of materials in an ultrahigh vacuum environment. The evaporant heating source can be either ohmic or a high current electron beam. Other common methods involve rf or dc sputtering, which are especially useful techniques when high film-substrate adhesion is required; chemical vapor deposition,

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which allows higher deposition rates than the usual sputtering or evaporation techniques; and, finally, we mention that anodization provides a way of making oxide films on metal surfaces.

Characterization of Films

Films can be characterized by usual metallurgical techniques which involve optical and electron microscopy, and x-ray and electron diffraction. More recently developed surface-sensitive techniques such as Auger electron spectroscopy,⁽¹⁾ secondary ion mass spectroscopy, and the spectroscopy of photoemitted electrons can be especially useful for very thin films. Also useful is the technique of Rutherford backscattering.⁽²⁾ In backscattering experiments, high energy particles are scattered from the film and an analysis of the energy of the backscattered particles allows a determination of the elements in the sample. This technique, as well as the surface-sensitive spectroscopies, has been developed to give a profile of composition as a function of depth into a film.

Structural Properties of Films

The structural properties of films are intimately connected with the properties of the substrate, deposition rate, gaseous impurities, and substrate temperature. With these variables available, unique materials and structures have been stabilized in films.

Probably the most dramatic structural changes in films involve amorphous or microcrystalline metals. These materials are made by depositing metals onto substrates that are cooled to the temperature of liquid helium which is 4.2 K above absolute zero.⁽³⁾ At these temperatures the metal atoms lack the thermal energy necessary for extensive diffusion, and extremely disordered structures can be obtained. In the case of Bi deposited at these temperatures it appears that the Bi actually is in an amorphous phase, since at some temperature near 30 K it rapidly crystallizes into its bulk structure.⁽⁴⁾ With other materials, grains gradually grow as the temperature is raised, and there is no sharp transformation. These films are probably composed of small grains having the same structure as the bulk material. Finally, it is worth mentioning that many phases can be formed in films that are either difficult or impossible to make by bulk metallurgical techniques. This particular aspect of films will be discussed later.

Another problem involved with film structure is the study of the interaction of metal atoms on various substrates and especially how this interaction affects the structural properties of the film. This constitutes the study of epitaxy⁽⁵⁾ and the related problem of film nucleation.⁽⁶⁾ In most cases the initial atoms hitting a substrate form small islands of metal about 20Å to 30Å in diameter. These islands then grow and at some stage they touch and

begin to coalesce into larger islands. As the large islands grow together, channels are formed which are then covered with newly deposited metal until a uniform film is finally formed. These studies have traditionally been made by using an electron microscope.⁽⁷⁾ In recent years low energy electron diffraction (LEED) has been used to study monolayers of metals on various substrates. This technique has shown that it is possible in certain cases to achieve uniform crystalline monolayers or near monolayers of a metal on a particular substrate. The fact that the diffracted electrons have low energy causes them to interact strongly with the specimen. In some ways this makes a cursory interpretation difficult, however detailed analysis of the intensity of LEED patterns can give detailed information about atomic positions on surfaces in some cases. A LEED pattern of an epitaxial thin metal layer is shown in Fig. 1.

Some Unique Physical Phenomena in Thin Films

Besides the convenience of using films in certain applications, there are phenomena which are best studied and are even unique to ultrathin films. Films, of course, provide a way of studying phenomena in approximately two dimensions. We say approximately since the effect of the substrate can be nontrivial. Both magnetic phase transitions and superconducting phase transitions have been studied in this quasi two-dimensional case.

Problems of nucleation and the film-substrate interaction are crucial in the interpretation of these results. For example, results on Ni films and iron-nickel alloys show that the magnetization and Curie temperature stay constant in films down to about 50Å thick. Below this value various investigators obtain different results, however the films are granular in this regime and there is no longer an ideal film geometry. In a similar way, experiments where Ni is grown epitaxially on Cu show no magnetic behavior below 7Å,⁽⁸⁾ although it is not clear what effect the copper substrate has. A similar situation is found when investigating superconducting materials. Below some critical temperature superconducting metals go into an ordered state where they have zero electrical resistance. As superconducting films approach thicknesses below about 50Å the transition temperature of some metals shows a large decrease.⁽⁹⁾ It is likely that the interaction with the substrate plays a role in the degradation of these superconducting properties. It should also be mentioned that phase transitions in two dimensions have been studied in rare gas films and in films of superfluid helium. The recent text by J. G. Dash⁽¹⁰⁾ serves as an excellent introduction to this area.

Another class of problems that are of interest involves changes in the transport properties of metal films due to the

film boundaries. If the films can be made thin enough so that the distance between internal electron scatterings becomes greater than the film thickness, it is clear that boundary scattering will greatly influence the transport properties,⁽¹¹⁾ and this field has been studied experimentally and theoretically for many years. The problem of how electrons scatter from film boundaries, and the effect of this scattering on transport properties has also been studied by using magnetic fields which bend the electron orbits away from the surface, causing a decrease in resistance. This effect has been observed in wires and films.

Another class of problems, somewhat related to the above, involves changes of the transport properties of films due to quantization of electron orbits in the direction perpendicular to the plane of the film. This effect is due to the wave nature of the electrons in the film and the fact that the electron waves must fit within the small dimension of the film in discrete units of the electron wavelength perpendicular to the plane of the film. Clearly if the film is much thicker than the electron wavelength this effect becomes negligible. However, in the case where the thickness is only a few wavelengths, this effect becomes significant. Since the characteristic wavelength for electrons in a metal

is only on the order of a few angstroms, or an interatomic spacing, this effect is difficult to observe. In Bi the situation is somewhat different since the films grow on mica in such a way that the electron wavelength perpendicular to the film is on the order of a few hundred angstroms. Films can be made conveniently in this range and the above effects of "size quantization" have been studied in this regime.

In this section we have tried to give some inkling of basic physical phenomena which can be studied with thin films. Of course, a discussion of many unique phenomena in films has been left out, such as the high field behavior of superconducting films, the optical properties of films, the use of films for studying materials by the technique of electron tunneling, the Josephson effect in superconducting films, the photovoltaic effect in films, adsorption and catalysis on films and many other fascinating phenomena.

Unique Materials Using Films

Perhaps the most important modern materials that involve thin film technology are the new multilayer structures involved in integrated circuits,⁽¹²⁾ where hundreds of components are placed on a silicon chip whose size is of the order of 2.5 mm x 2.5 mm. In some sense this is a unique material that is made by using films, and in fact these devices have revolutionized modern electronic technology. Nevertheless, nearly all the properties of these

devices can be understood in terms of the behavior of the bulk materials from which they are fabricated. The very clever thin film techniques used to make integrated circuits are primarily concerned with reducing device size.

A further important technological use of thin films is found in photovoltaic devices. Again the phenomenon itself is not unique to films, however it appears that the economic use of photovoltaic devices could well depend on film technology. The present approaches to photovoltaic devices manufacture involve silicon production technology and the technology of producing III-V and II-VI compounds.⁽¹³⁾ For GaAs, the absorption edge is much sharper than for silicon and whereas a wafer thickness greater than 10^{-3} cm is necessary for reasonable absorption efficiency with silicon, only about 10^{-4} cm is necessary for GaAs. Hence even though silicon is an intrinsically cheaper material it appears that polycrystalline thin film GaAs detectors can compete with silicon devices. These considerations are too detailed to be dealt with here, but they essentially involve the conditions on the grain size in these polycrystalline films in relation to their optical absorption lengths and charge-carrier diffusion lengths.

In concluding this section we briefly discuss materials that remain superconducting to the highest temperatures, and which promise to be extremely important technologically. These materials

have the A-15 structure, and Nb_3Ge , which has the highest known superconducting transition temperature at present, shows an onset of zero-resistance behavior near 23 K and, in some reports, as high as 25 K. Nb_3Sn , which is the easiest niobium based A-15 superconductor to make, has a transition temperature T_c of about 18 K. An interesting feature of these materials is that higher T_c 's appear in less stable materials. While Nb_3Sn can be made by various bulk metallurgical techniques, at present Nb_3Ge has only been prepared by deposition from the vapor phase onto substrates held at a high temperature.⁽¹⁴⁾ Various deposition techniques have been used successfully such as electron beam codeposition, sputtering, and chemical vapor deposition. A problem of further interest in this area is the question of whether high T_c Nb_3Si can be made and stabilized by various deposition techniques. There is speculation that if this material could be formed metastably with the proper A-15 structure, and close to a 3:1 niobium to silicon ratio, then a T_c even higher than 23 K could be achieved.

Summary

In this short article we tried to give some idea of unique phenomena that occur in films from the point of view of a solid state physicist. In concluding we should emphasize that films form the basis for many established and developing technologies. In the simplest case, metal layers have always been important for

optical coatings, and even as protective coatings for various materials. In the most sophisticated cases, films and their interaction on silicon surfaces form the basis of modern electronic technology. Furthermore films of silicon, GaAs and composites of these materials promise to lead to practical photovoltaic devices. It is fair to say that besides being a field of great interest in modern physics, the study of thin films also has contributed vital elements to the most sophisticated commercial technologies.

Figure Captions

Fig. 1. The LEED pattern from a PbTe single crystal substrate (Top) and an epitaxial Pb film (Bottom) grown on this substrate by evaporation of Pb. The Pb film is less than 15Å thick. The energy of the diffracted electron beam is 94 eV.

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