SVC Topics

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PVD Processes: Crystalline Structure By Diffraction Techniques

In some thin-film applications, such as films for magnetic recording media, the crystalline structure and its orientation are important to the active functionality of the film. In some applications, such as films used as diffusion barriers, the size of the crystalline grains in the film is important because grain boundary diffusion is generally much higher than diffusion through a crystal lattice. In many cases, non-reproducibility of the crystalline structure from run to run is an indication of the non-reproducibility of the PVD process being used. For example, uncontrolled energetic particle bombardment from high-energy neutrals from the sputtering target in sputter deposition can change the average grain size and preferred orientation of the crystal structure of the film. The variation in bombardment can be the result of pressure of differences from run to run. Impurity-atom incorporation can also cause changes in crystal structure or crystalline dimensions either by occupying a lattice site (substitutial atom) or by occupying voids between lattice sites (interstitial atoms). In the extreme, impurity-atom incorporation can cause changes in the atomic arrangement.

The various atomic arrangements possible to form crystals were discussed previously (*P&SF* **85**(3) p. 44, 1998). The periodic atomic arrangement in a crystal is defined by the number and species of the nearest neighbors to each atom (coordination number), and the distance and direction (bond angle) to each nearest neighbor. Each periodic atomic arrangement will produce atomic planes that will be characterized by a direction relative to other planes, a separation of atoms on each plane and an atomic density on each plane. Figure 1 shows a two-dimensional periodic array of points and the creation of planes in the array with various separations and varying densities of points on the planes.

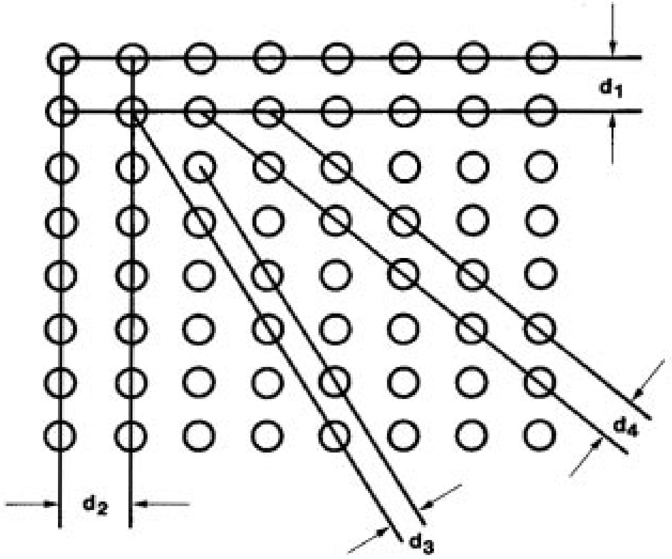

Fig. 1—Interplanar spacings and population of planes: Depiction of how a two-dimensional array of points can form planes, with specific spacing between planes, and showing how the aerial density of points can vary on each plane.

A diffraction pattern is generated by the constructive and destructive interference of waves diffracted from a periodic arrangement of diffracting sites shown in Fig. 2. The intensity of the diffraction signal will depend on the number of diffracting sites. For atomic arrangements—where the distance between atoms is small—the wavelength of the radiation must be small, so high-energy X-rays are commonly used to give X-ray diffraction patterns. Since particles, such as electrons and neutrons, have a wavelike component, they can also be used to form diffraction patterns.

Diffraction can either be from a three-dimensional array of diffracting sites or from a two-dimensional array, such as atoms on a surface, as shown in Fig. 2. To determine the arrangement of atoms on a surface or in a very thin layer near the surface, low-energy electrons (low-energy electron diffraction—LEED), small angles of incidence of the X-rays or reflected high-energy electrons (reflection high-energy electron diffraction—RHEED) can be used.

In Fig. 2, the conditions for constructive interference in diffraction are given by:

$$n\lambda = 2d \sin\theta$$

where λ is the wavelength of the incident radiation, n is an integer and d and the angle θ are as shown in Fig. 2.

When these conditions are met, the diffracted signal is the strongest. The higher the density of diffracting sites on a plane, the stronger the signal. The intensity of the diffracted beam can be determined using a number of different types of detectors. A common means is to use photographic film, which is sensitive to X-rays and electrons. The amount of exposure of the film is determined by the signal intensity. The photographic film can be placed in a circle about the sample so that all points on the film are an equal distance from the sample. The separation between the exposed points on the film is a measure of the diffraction angle. The relative intensities of the detected signals are determined using a densitometer. In general, the line separation and relative intensities from the densitometer are fed directly into a computer program that compares the pattern to a library of diffraction patterns from various materials and atomic structures to give the most likely structure and material. Another type of detector moves in an arc around the sample and measures the intensity of the diffracted signal electronically.

Single-crystal Material

In some cases, a material may be compromised of a single atomic arrangement and orientation. The material is called a single-crystal material. Usually, a crystalline material is comprised of many crystals (grains), each having some displaced orientation with another. This type of material is called a polycrystalline material. The very narrow band of material between each grain is called a grain boundary. Each grain may have from a few to many atoms in its structure. If most of the grains are oriented in some common direction, the direction is called the preferred orientation.

If a polycrystalline material is fragmented into small pieces and a diffraction pattern is taken of the powder ("powder pattern"), the relative intensities of the diffraction signals for each plane would be that of an isotropic distribution of grain orientations. If the pattern intensities from a polycrystalline material differ from that of the powder pattern, this is an indication of a preferred orientation in the polycrystalline material. The degree of preferred orientation and the direction of the preferred orientation can be determined by "pole-figure analysis." PVD-deposited films generally have a preferred orientation that may vary with deposition conditions, such as with or without concurrent energetic ion bombardment during deposition.

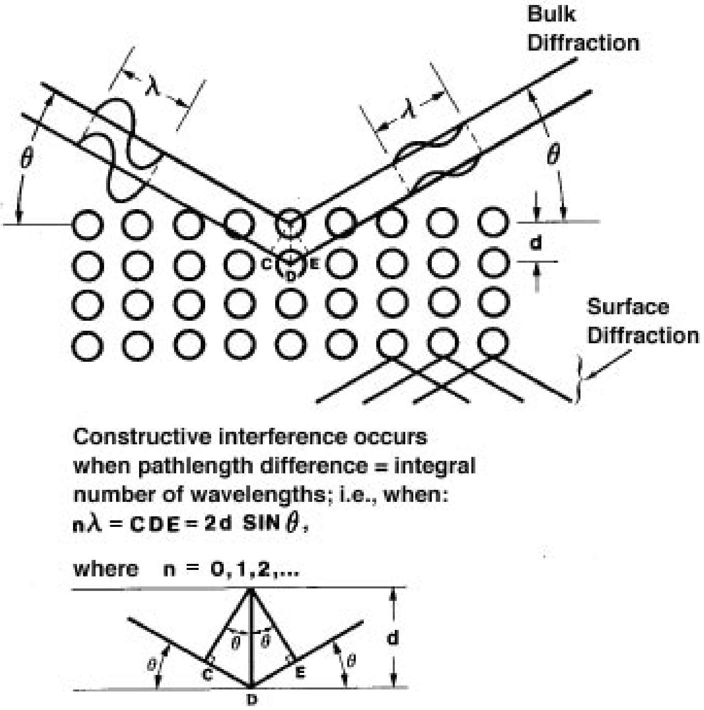

Fig. 2—Diffraction of radiation from a bulk crystalline lattice and from a surface array.

The shape of the lines in the diffraction pattern depends on the uniformity of the periodic arrangement and the number of diffracting sites. If the number of atoms on a plane becomes too small, the line will broaden as compared to the intensity and the line width found in the powder pattern. This decrease in intensity and line broadening can be used to determine the grain size if the grains are very small.

The crystal lattice can be strained and the d-spacing changed by applying a stress to the structure. A compressive stress will decrease the d-spacing in the direction of the applied stress, while a tensile stress will increase the d-spacing. The amount of stress can be determined by measuring changes in the d-spacing and knowing the elastic properties of the material. In PVD films, the film stress often changes with thickness of the deposited material, through the thickness of the film, and is often different in the plane of the film compared to that in the thickness-direction of the film. In addition, PVD films often have small grains and a high percentage of grain-boundary material whose properties cannot be determined by diffraction techniques. This makes determination of the cumulative stress in a thin film difficult to determine by diffraction techniques. A more general stress measuring technique for thin films is to use a cumulative-effect technique, such as the bending of a beam on which the film has been deposited (*P&SF* **81**(6) p. 144, 1994).

By using focused electron beams in electron diffraction and defining apertures in X-ray analysis, very small areas can be examined by diffraction techniques ("microdiffraction techniques"). In the transmission electron microscope (TEM), electron diffraction ("selected area diffraction") can be used to determine the structure of very small particles or areas of a film. P&SF