

Introduction

1.1. Introductory remarks :

That properties of materials depend to a major extent on how and which atoms are arranged in them is by now well established. Solid materials are divided into two groups — amorphous and crystalline with various shades of crystallinity lying in between. The ideal amorphous material is one in which atoms are distributed with perfect randomness. It is easy to see that such perfect amorphous materials are very difficult to obtain specially when the finite size of the atoms produce a local regularity of arrangements. Similarly, the perfect crystal is a material in which crystallographically identical atoms are arranged in a perfect three dimensional lattice. Again, a perfect crystal is very difficult to get. Perfect crystallinity breaks down because of various reasons, the simplest reason being, again, the difference in size between different types of atoms. Assuming the crude model of each atom being a hard sphere of a given radius and also assuming close packing of these atoms to give rise to the crystal, we easily see that introduction of atoms of different size in the lattice point of an otherwise perfect crystal will cause random displacement of each atom from its perfect lattice site. Thus, there appears to be a greater probability of breakdown of crystallinity in materials composed of more than one type of atoms as compared to materials which are monatomic. This departure from crystallinity is, however, very small and local in nature. This is a case of local disorder. It may be noticed that while perfect disorder as in the perfect amorphous state is prevented from

being realised by the local ordering caused by the finite size of atoms, the same factor viz., finite size of atoms prevents perfect order from materializing. It is obvious that local ordering is a very important factor in determining the arrangement of atoms in a material and thus, ultimately, in determining the physical properties of the given material.

Local disorder is a predominant factor on an interface between two media. Inside a perfect crystal, each atom is stable in its own site due to the interatomic forces between the given atom and its different neighbours cancelling each other. On the interface, atoms are subject to two sets of forces which are different from those acting on similar atoms inside either of the media. Hence it is extremely likely that the forces do not cancel each other when the atoms lie on their normal lattice sites. Equilibrium is, however, restored when the atoms have suffered relative displacements so that the forces acting upon each atom have changed both in magnitude as well as in direction. It is because of this reason that surfaces are sometimes considered as extended dislocations. Thus the arrangements of atoms on surfaces are expected to be different from those inside the bulk of the crystal. From the standpoint of measurements, when the surface to volume ratio is relatively small, measurements on atomic arrangements convey informations characteristic more of the bulk than of the surface. When, however, this ratio is large, measurements bring out informations mostly of the arrangement of atoms on surfaces. The ratio of number of atoms lying on the surface to that of atoms in the volume is considerable in the case

of thin films. Thus, a study of arrangement of atoms in thin films yields informations regarding arrangement of atoms on open surfaces. When the film has been deposited on a substrate and is extremely thin, atoms on the open surface are also subject to forces of interaction due to atoms on the surface of the substrate. The effect of this interaction becomes more and more feeble as the thickness and hence the distance between the open surface and the substrate surface increases. This will result in the distribution of atoms on the open surface being different at different thicknesses. Conversely, a study of thickness variation of atomic arrangements in a film on a substrate is expected to reveal the nature of interatomic forces between the open surface and the substrate. This consideration has led to the present investigation of structure variation with thickness for some metals and semiconductors.

It has already been seen that whenever more than one type of atoms occur in a material, there is a probability of local disorder taking place due to size difference between the atoms. The size difference results in atoms being pushed out of their allotted sites in the lattice and suffering random, albeit small displacements. Another type of disturbance in lattice arrangements takes place in such cases. Let us consider the simple case of a crystal containing two different types of atoms. In the mixed crystal containing the two types of atoms, the less numerous atoms may be considered to be guests in the lattice of the more numerous type. The way the guest atoms are distributed in the host lattice causes what is known as the order-disorder phenomenon. When the guest atoms occupy certain specific lattice sites in the host

lattice regularly, the mixed crystal is considered to have an ordered structure. When the guest atoms are distributed to occupy random sites in the host lattice, the structure of the mixed crystal is said to be disordered. Between perfect order and perfect disorder, there are various shades of partial order. Ordering is measured in terms of proportion of specific lattice sites occupied by a given type of atom or in terms of the probability of a nearest neighbouring site being occupied by a given type of atoms. The first sort of measurement gives what is known as long-range ordering while the second type of measurements gives the short-range ordering. Short-range ordering may exist in a crystal even when the long-range ordering is zero. Since short-range ordering is a measure of arrangement of nearest neighbours, it is automatically also a measure of local ordering. The short-range ordering (SRO) is different from size effect ordering (SEO) in the sense that the atoms are supposed to occupy sites in the ideal lattice. It is quite evident that in a real crystal both these effects will be co-existing. Thus, in measuring SRO, effects due to SEO will have to be taken into consideration and vice versa. However, in most cases, SRO is more apparent than SEO which is comparatively a less perceptible effect. For this reason, SRO has been measured in course of the present investigations in a well-known alloy viz., α -brass.

1.2. Method of Measurements

In the present work, an attempt has been made to study the local atomic arrangement i.e., lattice defects and ordering in metals, alloys and semiconductors in the form of thin films and