

SVC Topics

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PVD Processes: Atomic Arrangement

– n physical vapor deposition (PVD) processing, atoms that condense on the substrate surface may form an amorphous (glassy) phase where there is no long-range atomic arrangement-often designated with an "a" or an " α " (a-Se or α -B)—or they may form a homogeneous region where there is a specific long-range threedimensional repetitious atomic pattern called a lattice. This region is called a crystal or a grain, and each defined crystal structure is called a phase. In PVD technology the ability to form a crystalline phase rather than an amorphous phase may depend on the mobility of the atom on the surface. For example, deposition on a surface at a very low temperature may decrease the mobility of the atom, and cause the deposited film material to be amorphous whereas if the deposition was done at a higher substrate temperature, the material would deposit as a crystalline material. In many ways this is equivalent to rapidly cooling (rapid quenching or "splat" cooling) a liquid into a solid, which can result in forming an amorphous material.

A solid formed by condensation of atoms of a single material is characterized by the number of nearest atoms called the coordination number (CN), the distances to the nearest atoms and the directions (bond angles) to the nearest atoms. This, in turn, determines the fraction of the volume occupied by atoms, which is called the packing fraction (PF). Generally, atomic structures will try to maximize the packing fraction as much as the atom sizes and the bonding angle will allow. If there is crystallinity (long-range order). There

are a			
number of	System	Axes	Bond Angles
possible	Cubic	$a_1 = a_2 = a_3$	All angles = 90°
atomic	Tetragonal	$a_1 = a_2 \neq a_3$	All angles = 90°
arrange-	Orthorhombic	$a \neq b \neq c$	All angles = 90°
ments that	Monoclinic	$a \neq b \neq c$	2 angles = 90° , $1 \neq 90^\circ$
can be	Triclinic	$a \neq b \neq c$	All different, none = 90°
visualized	Hexagonal	$a_1 = a_2 = a_3 \neq c$	Angles = 90° and 120°
by	Rhombohedral	$a_{1}^{2} = a_{2}^{2} = a_{2}^{3}$	All equal, but not 90°
consider-		1 2 5	•
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stacking of balls and layers of balls, as shown in the figure. The basic atomic arrangement that is repeated is called the unit cell, and in most atomic structures the unit cells overlap and penetrate into each other.

The simplest atomic arrangement is the simple cubic lattice structure, but the three-dimensional packing fraction is low (PF = 0.52). More energetically favorable cubic structures are the face-centered cubic (fcc) (CN = 12, PF = 0.74) where an atom is located in each face of the cubic "box," or the body-centered cubic (bcc) (CN = 8, PF = 0.68) where an atom is located in the center of the cubic "box." Figure (d) shows bcc unit cells that interpenetrate each other, with each lattice site of one unit cell becoming a lattice site in another unit cell.

Another type of unit cell is the hexagonal unit cell where the unit cell is created by the rotation of a rhombic cell, as shown in Fig. (e and f). Penetrating hexagonal unit cells create the hexagonal close-pack lattice structure, as shown in Fig. (g), (CN = 12, PF = 0.74). In the hcp structure the atoms of one unit cell penetrate and reside in a hollow formed by three atoms in an atomic plane of the rhombic cell. Many pure

elements form cubic crystal structures, with some forming hexagonal close-packed (hcp) structures (e.g.. Be, Mg, Zn) and a few forming other structures. Some other structures are given in the table.

The crystallographic planes in a lattice are identified by their Miller indices, as shown in Fig. (h). The indices are the reciprocals of the distances along the axis where the plane intersects the axis. If the plane is parallel to an axis, for example, it will intercept it at infinity and the reciprocal will be 0. A plane parallel to the X and Y axis and intercepting the Z axis, therefore, will be the (001)plane. Planar direction is taken as the direction normal to the plane. By convention, the nomenclature for planes is given in parenthesis, such as (111), and planar directions are given in brackets, such as [111]. The twodimensional packing density of atoms varies in each plane.

In PVD processing, the growth of lattice planes is determined by the surface mobility of the atoms and some may grow more readily than others. This gives rise to a preferential orientation for certain atom planes in the film, even though the overall structure of the film is polycrystalline. The (111) planes of the grains, for





example, may be predominantly parallel to the surface of the substrate. This preferential alignment of lattice planes is called the crystallographic texture.

If the lattice orientation is the same throughout the material it is called a single crystal material. If different regions have the same lattice, but the regions have different lattice orientations, the material is called a polycrystalline material. A polycrystalline material may have grains with different crystallographic structures as well as different crystallographic orientations. The atomic separation, coordination number and angular distribution can be affected by the temperature of the solid to such a degree that in some materials there will be a different crystallographic arrangement at high temperatures compared to that at low temperatures. The relationship of the lattice arrangement to the environment (pressure, temperature, etc.) under equilibrium condition is depicted in an "equilibrium phase diagram" for the material. The phase diagram can also show the conditions at which the material changes from a solid to a liquid and from a liquid to a gas (vapor).

In film deposition sometimes the high temperature phase or a unique phase is "quenched in" during deposition, and the resulting crystallographic phase is metastable. This means that the crystallographic structure may easily be changed by mechanical stress or heating. Carbon in a diamond lattice, for example, can easily be irreversibly converted to carbon in a graphitic form by heating. Unusual crystallographic phases can be formed because of film stress or impurities incorporated into the lattice structure.

Amorphous and crystalline materials can be formed by the condensation of two or more different atomic species such as titanium and nitrogen, which chemically react to form crystalline TiN or silicon and hydrogen to form amorphous silicon (α -Si:H). In some cases the same composition can form either an amorphous (glassy) phase or a crystalline phase. Silicon and oxygen, for example, can form crystalline quartz (SiO₂) or fused silica (α -SiO₂), a glassy phase that has a short-range order between the silicon atom and the two oxygen atoms but has no long-range order. In the case of crystallinity, the atomic arrangement is affected by the relative number and size of the atomic species that bond together. For example, there are different atomic arrangements for the crystalline compositions of ferrous oxide (Fe₂O₄--the mineral magnetite) and ferric oxide (Fe₂O₂--the mineral hematite). In reactive film deposition this chemical composition of the film material can be determined by the chemical activity and availability of the reactive species during deposition. Solubility is the ability to disperse

atoms of a material (solute) in a matrix of another material (solvent) without causing a change of crystallographic structure of the matrix material, and without causing the solute to precipitate as a separate phase. Such a combination is called an alloy. The solute atoms may occupy lattice sites and are called substitutional atoms, or they may occupy voids in the lattice structure and are called interstitial atoms. There may be unlimited solubility of one material in another such as lead and tin, or there may be a limited solubility above which the excess solute material will precipitate out as a second phase. For example, 10 wt pct of SnO_2 is soluble in In_2O_2 . Above that amount, the excess SnO₂ will precipitate as a separate phase. The alloy of 90 wt pct In₂O₂ and 10 wt pct SnO₂ is a common form of indiumtin-oxide (ITO) used for transparent electrical conductive films. The equilibrium phase diagram for two or more materials can show the effects of chemical composition and temperature on the composition and relative amounts of phases that are formed. Normally in thermal processing, such as melting, when the solubility limit is reached, the second phase will precipitate out readily. In PVD processing it is possible to have an atomic dispersion of the solute atoms in the matrix in amounts far above the equilibrium solubility limit. This metastable combination is called a mixture. PASF