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THE BASIS OF PHYSICAL CHEMISTRY, PROPERTIES OF TWO-DIMENSIONAL SOLIDS

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Abstract

Advanced surfaces provide opportunities to develop new surface materials and surface technology. The recent development of hyperfine surface structure - clean surface, thin films and nanophase structures – as well as sophisticated analytical tools, opened up atomic/molecular studies of surface phenomena and new application.

Introduction

Today materials science is an interdisciplinary science. It include physical, chemical and engineering processes from microscopic to atomic levels. Sophisticated analytical instruments and theoretical understanding of materials has shown three important points: a.- material has a structure (a particular arrangement of internal components), b.- material have a range of properties (characteristic responses to external stimuli) and c.- by processing through nonequilibrium state it is possible to change a materials properties.

The physical chemistry is the border line subject between pure physics, chemistry and material science. Since the first scientific journal on the subject (*Zeitschrift fur Phsicalische Chemie*, 1887) it start to be an interdisciplinary science applicblle to the problems of physics, chemistry and material science. For all of these sciences, surface properties remain the most interesting subject of research and applications.

Surface science does not have such a long history as material science[1]. The birth of surface science can be the fact studied in 18th century by B. Franklin – the spontaneous spreading of oil on water. The use of surface chemical processes (catalysis, J. Dobereiner, G. Kirchhof, J. Berzelius) began in the early years of the 19th century. The studies of tribology, coincide with the industrial revolution when moving parts became prevalent. (Some understanding appears at 16th century - Leonardo da Vinci). The existence of polyatomic or polymolecular aggregates- colloids – was described by T. Graham, in 1861.

Thin solid films on surface were first obtained by electrolysis and chemical reactions. The first evaporated thin films/coatings were obtained by M. Faraday in 1857, when he exploded the metal wires in inert atmosphere. Crooks discovered the possibility of sputter-deposition of thin metal films in glow-discharge tube. In 1903 A. Wehneld discovered that poorly emitted metal cathodes when coated with barium or other alkaline earth oxides produce current million times greater than uncoated metal. In 1914 I. Langmuir and W. Roger showed that tungsten wire containing a little

thorium – after a heat treatment – could emit a current 10^5 times higher than pure tungsten at the same temperature.

The scientific curiosity in the properties of **two-dimensional solids** has led to the development of different types of surface materials. Recent development of hyperfine surface structures - **clean surfaces, thin films and nanophase structures** - opened atomic/molecular studies of surface phenomena and new applications[2].

Clean surface

In characterization of solids, the most important area of interest is to define the state of the surface – a **market discontinuity** from one material to another. At the beginning, surfaces are modeled as *sharp discontinuities*. In 1866, H. Sorby found that the *crystalline structure* of fractured surface depends on chemical composition and thermal treatment. *Terrace model* (1950) revealed that the surface is rough. *Clean surface* has been studied from 1960 when ultrahigh vacuum system and new experimental technique, made possible the molecular and atomic level investigation. Low energy incident beams provide a unique opportunity for investigation of physics and chemistry with surfaces. Such experiments bridge the gap between chemisorption and adsorption ($E < 5\text{eV}$) and sputtering and implantation ($E > 100\text{eV}$). Depending on the energy of incoming particles or chemical environment the surface atoms move/adjust their position on the bulk. In characterization of any real surface the **surface depth** is defined by the choice of characterization method – from one atomic layer to few microns[3].

Surface materials can be divided in *two groups*: those that utilize **external surface** and **microporous materials** where most of the surface resides in internal pores. Surface atom concentration may vary depending on the crystal structure and crystal face also. The *concentration of atoms/molecules* at solid surface can be estimated from the bulk density. For a bulk density of water/ice of 1g/cm^3 , the molecular density is $5 \cdot 10^{22} \text{ mol/cm}^3$. The surface concentration assuming cube-like packing $C = \rho^{2/3} \approx 10^{15} \text{ mol/cm}$ [4].

Clean surfaces are fastly covered with particles from surrounding atmosphere. From the kinetic theory of gasses, the flux F of atoms/molecules striking the surface of unit area at ambient pressure P is given by:

$$F = \frac{N_A \cdot P}{2\pi MRT} \quad F(\text{at} / \text{cm}^2 / \text{s}) = \frac{3.51 \times 10^{22} \cdot P(\text{Torr})}{[M(\text{g} / \text{mol})]^{1/2}}$$

where: M is the average molar mass of gaseous species, T – temperature in Kelvin, N_A – Avogadro's number and R – gas constant. Using the value for nitrogen molecule for which $M = 28 \text{ g/mol}$, room temperature $T = 300 \text{ K}$ and Avogadro's number $N_A = 6,02 \cdot 10^{23} \text{ molecules/mol}$ one obtains $F = 10^{15} \text{ molecules/cm}^2/\text{s}$. To keep the surface clean for 1s or 1h the flux of incident particles (atoms/molecules) must be less than 10^{15} or $10^{12} \text{ particles/cm}^2/\text{s}$. At UHV conditions ($1,33 \times 10^{-7} \text{ Pa}$) it takes 10^3 seconds before a surface is covered completely with the particles from ambient forming an interface.

The *residence time* of an adsorbed atom on the substrate is given by $\tau = \tau_0 \exp(\Delta H_{ad} / RT)$

where τ_0 is correlated with surface atom vibration times (10^{-12} s). The surface concentration σ at/cm² of adsorbed particles on clean surface: $\sigma = F\tau$, where F is the incident flux.

Microporous materials have very large internal surface area. Crystalline alumina silicate (zeolites) have ordered cages of molecular dimensions where molecules can adsorb. Graphite and coal have porous structure with pore diameters $10^2 - 10^3$ nm and very large surface area (100-400 m²/g of solid). Bones of mammals (made of calcium apatite) have highly porous structure with pore diameters of 10 nm.

For theoretical considerations when the surface is covered with 10^{15} atoms/cm² we usually say that the surface is covered with **monoatomic layer**. However, it is not the case. The atoms of the deposited layer are never distributed as a monoatomic layer. They diffuse and form three dimensional nucleus and clusters. Particles of finite size are described as *dispersion* D ($D = N_s/N_{tot}$ number of surface atoms/total number of atoms, Fig.1). Only for small nucleus D is unity, while for cluster D decreases with the number of atoms.

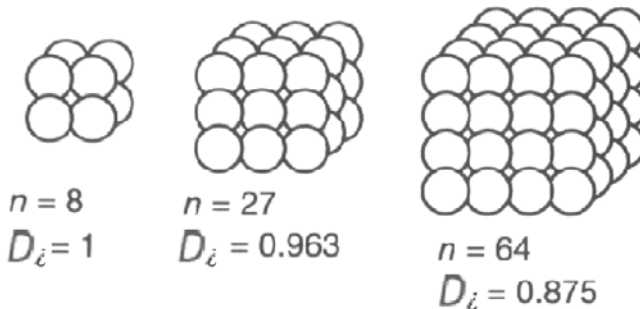


Fig.1. Number of atoms in the cluster (cubic crystal).

Finally, we must point-out that surface structure differs from the bulk structure. Three phenomena occur at clean surfaces: relaxation, reconstruction and modification [5].

Relaxation. By relaxation of metal surfaces, the first layer of atoms moves inward and leads to a shortened interlayer spacing between the first and second layer of the surface (Fig.2). On rough surfaces, the atoms relax in order to smooth irregularity. At ionic crystals, two ions move in a way that the positive and negative ions are almost coplanar.

Reconstruction. The atoms at the surface move not only perpendicular but also in the parallel direction. This often leads to new unit cells. Surface structure of Pt, Au and Ir (100) that should have square unit cells reconstruct to form hexagonal surface unit cells.

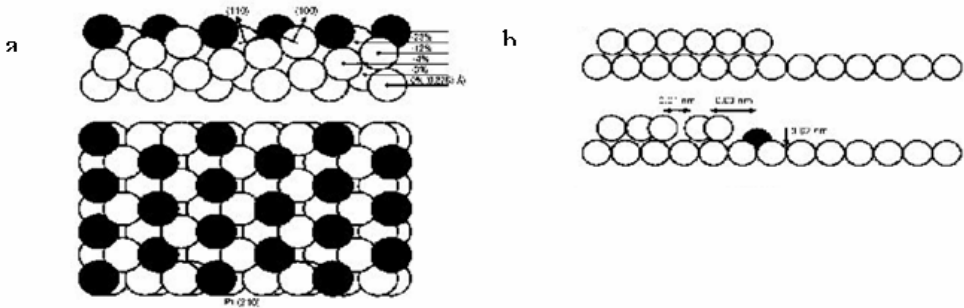


Fig. 2 (a and b). a- Relaxation at the clean crystal surface Pt (210), b- Restructuring at a step site; each atom attempts to optimize its coordination.

Modification. When energetic particles strike a solid surface, many kinds of interactions occur: desorption from surface, deposition of beam particles, the emission from solids, projectile implantation and momentum transfer to the target atoms[6]. All these processes are energy dependent and lead to a relocation of target atoms (Fig.3).

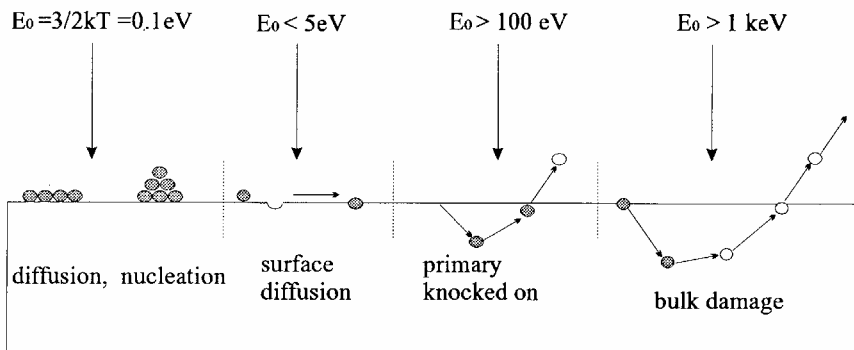


Fig.3. Simplified comparison of the incident particle path for: a and b – low energy beam, c- medium energy beam and d- high energy beam activated reaction.

Hyperthermal particles arriving at the surface dissipate their energy within a small area. Adsorbed particles can migrate over the surface and then aggregate. For higher energies, beam surface modification processes are important. Penetration depth of the beam particles into material allows modification of the materials due to requirements.

Chemical sputtering with small energies is observed, when the impinging particles react with target atoms producing a volatile chemical compound.

Physical sputtering occurs at incident energies of few hundred eV and higher [7]. Low-energy beams, with the incident energy E_k of the order of a few tens eV, can be used for direct film deposition on surfaces if two conditions are satisfied: 1. the

atom/ion sticking probability is higher than the sputtering probability, and 2. the reaction product is not volatile.

Surface modification technique has been applied mostly in semiconductor technology. Implantation of Y into the near-surface region improves the mechanical properties and the resistance to oxidation of stainless steel; implantation of N₂ reduced the coefficient of friction and increases the hardness of surface. The ion beam processing can alter biomaterial characteristics also (surgical implants).

Thin films

Thin film studies have advanced many new area of research. A number of methods have been developed—physical and chemical vapor depositions, electroplating and spraying—to prepare thin films/coatings of different types of materials. *Properties* of deposit depend on starting material, method used, vacuum, deposition condition, properties of the substrate and final thickness. The fundamental relationships between processing parameters and microstructure, as well as between microstructure and thin film/coating properties are important to determine the system quality and actual applications.

Physical and chemical vapor depositions are the most commonly used methods for deposition of different type and structure of thin films. Since the gaseous material-evaporated and sputtered- are very sensitive to the presence of impurities it is necessary to work at high vacuum condition to obtain high-quality thin films/coatings.

The *deposition* of thin films/coatings in vacuum consists of *several steps*: transitions of solid or liquid phase in the gaseous phase; transport of gaseous material from vapor source to substrate at low pressure; condensation of vapor phase on the appropriated substrate.

The first *characterization of thin film* structural characteristics includes the analysis of homogeneity as a function of thickness of deposited material[8]. Four stages characterizing the distribution of condensed material are mostly evident. The first stage (up to 10 nm for Au) consists of three-dimensional islands. By further deposition the islands grow, the nuclei coalescence and empty channels (with 5-20 nm) randomly distributed on the substrate are formed. If the thickness is higher than 30 nm (for Au, depend on materials T_m) a thin film is continuously deposited on the substrate. Microstructure, sizes, shapes and orientation of crystal grains and morphology of the surface material are strictly thin film phenomena, depending on deposition parameters and substrate properties (Fig. 4).

Depending on the physico-chemical properties of the substrate and the deposition parameters, various type of growth can occur: island growth (Volmer – Weber mechanism); layer growth (Frank – Van der Merwe); and island - layer growth (Stranski – Krastanov). The microstructure of coatings may vary from defect free single crystals (on single crystal substrate) to highly columnar and faceted structure.

The major application of thin film components is in integrated thin-film networks. Circuits consisting of thin film resistors (NiCr), capacitors (Ta₂O₅), contacts (Al, TiPd, Au), and interconnections are produced for different purposes

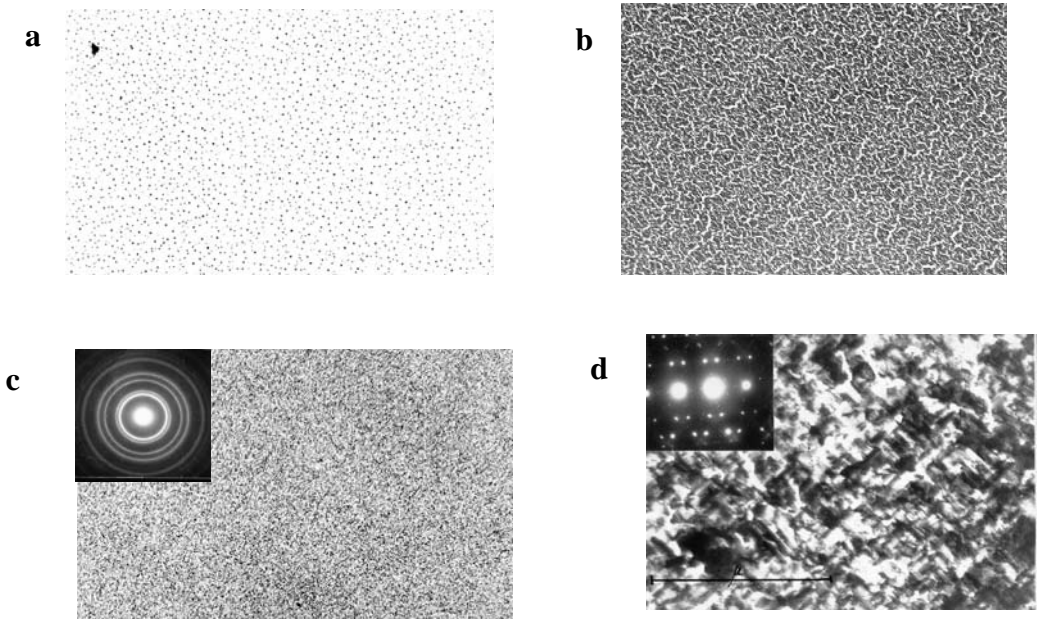


Fig.4 (a – d). Steps of the thin film/coating growth presented schematically: a-formation and coalescence of islands, b-the large islands growth, c-the channels and holes, d-continuous film/coating.

A large variety of deposited thin films/coatings grown by PVD technique has the high level of application: optically functional thin films (mirrors and lenses), energy transmission thin films/coatings (solar absorbers architectural glass), electrically and magnetically functional thin films (active devices, photovoltaic solar cells) mechanically functional coatings (hard, tribological, lubricant), chemically functional coatings (corrosion protective, thermal barrier) and decorative coatings (jewellery, toys, papers). The most frequently investigated mechanical properties of thin films/coatings are their adhesion to substrates, mechanical stresses and their tensile properties.

Nanophase structures

The properties of material are not determined only by chemical composition, alloying, cold working, annealing or deposition method. Ordered array of atoms and idealized structures can not explain all observed material properties. *Unique properties are based on deviation from ideal crystal structure.* It was found that fine grain size, presence of crystal of second phase or repetitive structure of deposited thin films improve material properties. The interface between individual grains, different phases or deposited layers, act as barriers to the motion of dislocation and are mainly responsible for plastic deformation of crystalline solids. Fine grain material is harder and stronger because surface/interface atoms are not bonded to the

maximum number of neighbors and are in higher energy state than interior atoms. The dependence of yield stress σ on the grain size varies approximately according the relation:

$$\sigma = \sigma_0 + kd^{-1/2},$$

where σ_0 is applied stress, k and d are constant for particular material.

The necessity for more efficient uses of materials invites a close look at **nanophase structure** of materials. Nanoparticles represent surfaces in three dimensions. The explosion of scientific and industrial interest in these materials arises from their properties.

Fine grain size – less than 10 μm to few nm – are produced by many methods: superplastic forming (from prealloyed fine powders), hot isostatic pressing (explosion), mechanical alloying (welding in a high-speed ball mill), rapid solidification (splat cooling and laser-glazing) and some other techniques.

Nanostructured materials may be defined as materials whose structural elements have dimensions in the range from 1 nm to 100 nm [9]. *Nanocrystal* is a fragment comprising between a few and few tens of atoms. The cluster synthesis can be done by: gas-phase synthesis (clusters are formed in the gas phase and than deposited - Ag cluster on graphite); self-assembled clusters on surfaces, Stranski – Krastanov and Wolmer – Weber growth (GaAsAl sandwich, vertical InAs nanocluster on GaAs) and colloidal synthesis of nanoclusters (Au and Ag colloids, cluster-cluster and cluster- surface interaction). The advances in nanocrystal synthesis have been made in: development of techniques for obtaining nanocluster of various compositions, passivation of cluster surface and for their assembly into well-ordered nanostructured solids.

The **properties of nanophase materials** depend not only on crystal size, but also on crystal surfaces and grain boundary characteristics. In this region dislocation change the direction of motion and the slip planes must overcome this discontinuity. The critical stress σ_c required to move a dislocation across the interface is given by: $\sigma_c = (\mathbf{E}_A - \mathbf{E}_B) / (\mathbf{E}_A + \mathbf{E}_B)$.

There is repulsive forces that increase as dislocations in a layer with smaller modulus (the ratio stress to strain) E_B approach the interface with the layers with larger modulus E_A .

It has been suggested that a high strength material could be obtained by deposition of layered structure of two materials with the same crystal structure [10]. Soon after, by deposition of two thin films TiN/NbN with nanometric thickness, superlattice structure of high hardness was obtained. **Superhard superlattices** are characterized by bilayer repeat period λ (Fig.5.). The material is scientifically and technologically very interesting. Hardness of TiN/NbN with $\lambda = 4,6$ nm is almost equal with highest hardness cubic BN (50 GPa). The structure of deposited TiN/NbN is easily produced by sputtering.

Two hardest known materials diamond ((80 – 100 GPa) and BN (50 GPa) have many applications (tribology, protection of engine components and cutting tools). However, diamond is etched by O_2 in air at high temperature. Sintetizing of cubic BN is difficult. New methods (three-dimensional surface science) provide opportunities to replace naturel materials with manmade materials.

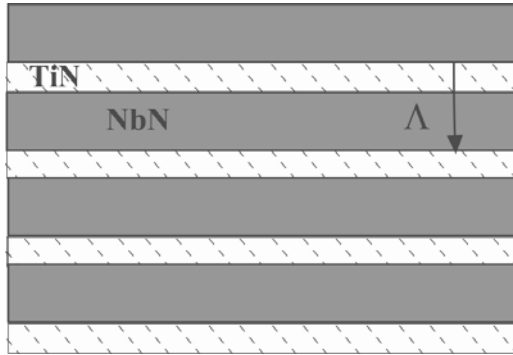


Fig. 5. Cross-section through a single-crystal superhard superlattice TiN/NbN with bilayer repeat period $\lambda = 5$ nm.

Comparing with crystalline material of the same composition, nanophase structures have lower density about 10 – 25%. The crystallites of nanophase materials have polygonal or lens shaped structure and their physical characteristics can be easily calculated: constituent volume $V = \pi d^3/6$, surface area $P = \pi d^2$, mass $m = \pi d^2 \rho/6$, molar mass $M = N_a \pi d^2 \rho/6$ and molar volume $V_m = MV/M$.

Conclusion

Hyperfine surface structure stands as a critical element in the resolution of the problem of the finiteness of resources, the scarcity of strategic materials and competitiveness in the market. The obtained results in advanced surfaces and materials are the basis of research into smart structures and intelligent material systems. No results have been published yet on smart and intelligent functional system, although some components of such system have been demonstrated. A complete smart material system would contain: sensor, actuators, signal processors, communication network and energy source. Many technological problems need to be overcome before applications reach the market.

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