

HYPERFINE SURFACE STRUCTURE

HIPERFINA STRUKTURA POVRŠINE

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In the characterisation of solids, the most important area of interest is to define the state of two-dimensional solids, their surfaces and interfaces. Since no change that occurs in nature is ever instantaneous and any real surface or interface must have a finite depth, the characterisation of any real surface or interface must take this depth into account.

Surface materials can be divided into two groups: external surface and microporous materials. In both cases the surface structure differs from the bulk crystal structure. Two phenomena occur at a clean surface: relaxation and reconstruction. During the relaxation of a surface the first layer of atoms moves inward and this leads to a shortened interlayer spacing between the first and the second layer. Furthermore, the atoms also move in a direction parallel to the surface and this often leads to surface reconstruction and the formation of new unit cells.

When clean surfaces are covered with deposited materials, the structure and the properties of the surface are altered as a result of interactions. All these processes are energy dependent. A low-energy beam can be used for the deposition of beam particles, desorption due to bombardment and chemical sputtering. For higher energies, beam-surface modification, emission from solids, projectile implantation and momentum transfer to the target atoms are significant processes.

In this paper the results of surface structure and properties are studied. For a low-energy beam these include the growth, structure and properties of thin, solid films, as well as the implementation of solid surfaces with deposited coatings. For higher-energy beams - ion beam, laser beam and fast oxide particles - the surface modification processes are discussed. It was found that whatever the mechanism of modification is, a similarity between erosion mechanisms does exist - the same energy and angular dependence. However, the topographic evolution of bombarded surfaces differs.

Key words: advanced materials, semiconductors, surface structure, clean surface, thin films, nanophase structures, characterisation of solid surfaces

Pri karakterizaciji trdne snovi je najvažnejša naloga definicija dvodimenzionalnega stanja njihove površine in mejnih površin. Ker ni nobena naravna sprememba skokovita in ima vsaka površina in mejna površina končno globino, mora karakterizacija to globino upoštevati.

Površinske materiale razdelimo lahko na tiste z zunanjo površino in mikroporozne. V obeh primerih je struktura površin drugačna od kristalne strukture matice. Na prosti površini se dogodita dva pojavi: relaksacija in rekonstrukcija. Pri relaksaciji površine se prvi sloj atomov pomakne v notranjost, kar ima za posledico zmanjšanje razdalje med prvo in drugo plastjo atomov. Atomi se tudi premaknejo vzporedno s površino, kar često vodi k rekonstrukciji površine in nastanku novih celičnih enot.

Ko se čista površina prekrije z nanosenim materialom, se struktura in lastnosti površine spremenijo. Vsi procesi so odvisni od energije. Maloenergijski snop se lahko uporablja za nanos delcev, desorpcijo in kemično naprševanje. Za velike energije snopa so značilne spremembe površine, emisija trdne snovi, implantacija delcev in prenos momenta v atom tarče.

V tem članku so predstavljeni rezultati raziskav strukture in lastnosti površine. Pri maloenergijskih snopih obravnavamo rast, strukturo in lastnosti tankih plasti ter nanos pokritij. Pri velikoenergijskih snopih pa obravnavamo ionski in laserski snop ter hitre oksidne delce in spremembo površine. Ugotovljeno je, da obstaja podobnost med mehanizmom erozije zaradi različnih procesov, enaka energijska in kotna odvisnost, drugačna pa je topografska evolucija obsevanih površin.

Ključne besede: napredni materiali, polprevodniki, struktura površin, čista površina, tanke plasti, nanostrukture, karakterizacija trdnih površin

1 INTRODUCTION

There has never been a period in history during which the evolution of materials has been faster and the range of their properties more varied than today. The development of crystalline materials has shown that the properties of materials are structure sensitive and that the microstructural features are determined by chemical composition and processing¹. New uses of conventional materials have yielded benefits for both the manufacturer and the consumer. Sometimes the decisions involved when choosing a material are less to do with materials than they are about forming, processing and surface state².

Materials science has a long history. The first period was the age of anonymous science. This was followed by the Stone Age and the era of metals. Interest in "new

materials and advanced material technology" began in the eighth millennium BC when human beings found that a piece of watered clay could be shaped into a pot and then hardened by fire.

The traceable history of materials science began later and can be divided into three main periods. First, is the active Greek period, from 600 BC to about 500 AD. The man traditionally associated with the beginning of science, Thales of Miletus, made certain geometrical discoveries - elementary mathematics. Greek philosophers from the 4th century BC (Leukip, Demokrit and Lucrecie) speculated that all materials consisted of small indivisible particles of the same substance (Demokrit - atoms). Aristotle (about 420 BC) supposed that all material things are composed of four elements - earth, air, fire and water.

The second period is the active modern period from about the 16th century to the middle of the 20th century. Mediaeval knowledge of the material world was essentially based on experience. With improvements in experimental techniques such as balances (Z. Jensen), lenses (A. Leeuwenhoek) and the microscope, as well as letters and the advent of printing, the scientific method became established. The works of Georgius Agricola (*De re metallica* 16 c.) and Francis Bacon (*Novum organum scientiarum* 17 c.) provide details on how to make an alloy, how to harden a metal and how to produce a theory. Nevertheless, materials were too complicated.

The first real understanding of materials developed in the 18th (A. Lomonosov, A. Lavoisier, L. Galvani) and 19th (J. Dalton, A. Avogadro, M. Faraday, D.I. Mendeleev) centuries. Chemical analysis came to be an essential tool for choosing and processing materials. H.C. Sorby introduced a new tool in his studies of steel - the light microscope (1866) - and concluded that the crystallinity of a fractured surface depends on the chemical composition and the thermal treatment. In time, the optical microscope was followed by new microscopes that could resolve details of microstructures, provide three-dimensional surface information and make an analysis of secondary emitted particles from the surface.

The basic contribution of the new analytical tools for studying materials was being able to relate a material's external properties to its internal structure and to an atomic level understanding of materials' surfaces and surface processes³. Three events contributed to the development of surface atomic/molecular sciences: advances in ultra-high-vacuum technology that permitted the study of clean surfaces (at 10⁻⁹ torr and better); the discovery of the transistor (1948 J. Barden, V. Brattain and B. Shockley) that resulted in the miniaturisation of components and an increase in the speed of electrical signals; and a demand for components that are critical to the successful operation of complex systems, including: electronic devices, aerospace research and transportation.

Sophisticated analytical instruments and a theoretical understanding of materials has shown three important points:

- A material has a structure, a particular arrangement of internal components. The subatomic structure gives us the locations and densities of the electrons and the nucleus with their mutual interactions. The next level is the organisation of atoms or molecules in the lattice of a crystalline material. Large groups of atoms with identifiable characteristics are individual grains. These groups agglomerate to form the microstructure and the macroscopic structural elements.
- Materials also have a range of properties that define their characteristic responses to external stimuli.

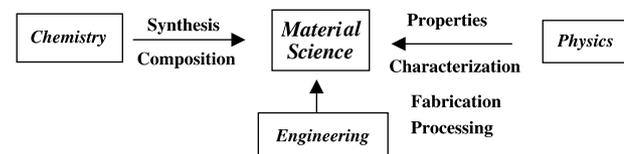
Electrical properties represent the response to the stimulus of an applied electrical field. Mechanical properties relate to an applied load and deformation. The relations between structure and properties determine the behaviour of materials and their performance.

- By changing the internal structure of a material, using non-equilibrium processing, it is possible to change a material's properties. However, of all induced changes, the most important point is to define the discontinuity - the surface and the interface - from one material to another.

2 ADVANCED MATERIALS

Today, materials science is an interdisciplinary science. It includes physical, chemical and engineering processes from microscopic to atomic levels (**Table 1**).

Table 1: Materials science



Advanced materials science 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. Materials scientists and engineers are developing advanced materials and processing methods that require little reliance on imported materials and yield products that are more efficient.

2.1. Advanced metals

With the aid of new analytical tools and processing techniques, scientists have created and exploited irregularities in metallic crystalline structures to make exceptionally strong alloys that resist heat and corrosion. With newly developed analytical techniques investigators found that it is the defects in the lattice that usually play the dominant role in such properties as a metal's ductility, brittleness and high-temperature behaviour. Metals in which it is difficult for a dislocation to move through an ordered crystal tend to be hard materials⁴.

Alloys that have been developed to cope with extreme conditions are known as superalloys. The key to the hardness of superalloys is the presence of a small amount of another metal or phase in which it is difficult for a dislocation to move. The most promising superalloys are nickel-based superalloys - for example, Ni₃Al (with 0,2 w% B) - in which small cubic crystals of γ' phase with 3 Ni atoms for every Al atom are embedded in a γ matrix phase in which an atom may occupy any

state. These materials do not have such good properties at very high temperatures. Cobalt-based superalloys that are strengthened by tungsten and molybdenum carbides collected at the grain boundaries of the crystals, although not as strong as nickel alloys, retain their strength up to much higher temperatures. The two phases of titanium-based superalloys with α -phase lens-shaped crystals and a β phase matrix are also somewhat restricted by a low working temperature of $\frac{1}{2} T_m$.

Advanced techniques for processing metals are as important as advanced alloys. One of the most important of these techniques is directional solidification (F. L. Versnyder and R. W. Guard, 1960). A material's resistance to creep can be increased dramatically if samples are made in such a way that all the grain boundaries are parallel to an applied uniaxial stress. Another advanced processing technique is superplastic forming, where metals are processed in such a way that the grain sizes are less than 5 microns. However, the processing technique that has caused the most interest is rapid solidification, which has cooling rates for the molten metal of about a million degrees/s. The most versatile techniques for material implementation employ different energetic beams (e^- , I^+ and $h\nu$). Low-energy beams are particularly important for the deposition of thin films and protective coatings. Using a high-energy ion beam we can introduce different atoms in chosen substrates⁵. A high-power-density laser beam can modify the surface microstructure without affecting the underlying surface, a process often referred to as laser glazing.

2.2. Advanced ceramics

Ceramics are crystalline compounds with ordered atomic arrangements, often between metallic and non-metallic elements. The bonding between atoms is usually ionic or covalent, making them more directional and rigid than metallic bonds. Chemical composition and microstructure determine all the macroscopic properties of ceramics. The strengths of the bonds in ceramics determine the chemical stability, the high melting point, the hardness and the stiffness. Unfortunately, the strength of the bonds prevents planes of atoms from sliding and ceramic materials cannot deform to relieve the stress imposed by a load.

Advanced ceramics are hard, resistant to both heat and chemicals and can be designed to have special electrical properties. Research is focused on a major problem, the tendency of ceramics to crack easily. The process for making advanced ceramics is similar to the traditional process, except that organic polymer binders are added instead of water⁶.

Since microscopic defects - voids, agglomerations and chemical impurities - are the sites where cracks originate, most of the research, involving the introduction of zirconium or fine ceramic fibres in a

ceramic or glass matrix, has been directed at eliminating such defects.

Individual ceramic devices could be used to sense temperature, pressure, light, heat, as well as certain chemicals, and could be coupled with a microprocessor to control machines in homes and factories. Particular areas of growth include: piezo-electric ceramics, the development of ferrite magnets for magnetic core memories in high-speed computers and silica-based optical fibres for telecommunications. In addition, ceramics are incorporated into internal combustion engines to allow higher operating temperatures and lower engine weight, which results in higher efficiency.

2.3. Advanced composite

Composite materials are the fastest-growing area of advanced materials. The term composite refers to a matrix that is reinforced with fibres, whiskers or a dispersion of another material. A number of composite systems have been devised: polymer-matrix, ceramic-matrix and metal-matrix composites.

The controllable microstructure of a composite allows it to be tailored so as to enable the distribution of stresses to which it will be subjected. The properties of advanced composites depend on the matrix, the reinforcing material and the geometry of the reinforcement. Interest in the development of advanced composites is guaranteed in the aerospace industry, military applications, car production and sports equipment.

2.4. Advanced polymers

The polymer molecule is built from smaller molecular units, or monomers, repeated a hundred or more times in a chainlike structure⁷. In the middle of 20th century most polymers were limited to their familiar role as inexpensive plastics, insulators or packing materials in electronics. More recently, however, advanced polymers have taken on new roles: strong reinforced fibres with a high degree of orientation, photoresists or electron-beam resists and biological molecules for particular uses.

Four factors relating to polymer chains critically affect the physical behaviour of the bulk polymer material: the average length of the chains, the strength of the forces among the chains, the regularity with which the chains are packed together and the stiffness of the individual chains. Fibre-reinforced polymer composites are synthetic copies of structures found in nature. Such composites have the ideal characteristics for use in aircraft industries.

2.5. Semiconductors

The most critical family of advanced materials from the technological and economic point of view is the

semiconductors, and the most familiar devices produced from semiconducting materials are the bipolar (BP) and field-effect (FET, MOSFET) transistors. Since the transistor's invention the small feature size and the projected pattern size have decreased from a line width of 30 μm in 1960 to much less than 1 μm today, and the level of integration has increased ⁸.

When transistors and computers started to become interesting in 1950, the interest in material and surface science shifted to the semiconductor materials of column IV of the Mendeleev periodic table - silicon (Si) and germanium (Ge) - and later to the combination of two elements from column III and V (GaAs, InP) or from column II and VI (CdS, ZnTe).

The electronic energy structure is the key factor in the design of semiconductor devices. In a semiconductor, the valence electrons are not strongly bonded to atoms and the band gap at low temperatures is small. Therefore, a small amount of energy is needed to induce a current. The promotion of an electron into the conduction band can be realised by thermal oxidation or by a small concentration of impurities in the semiconductor. When Si is doped with a small amount (10^{-12} atoms/atom) of an element from column V (P, As), the resulting alloy contains free electrons. Doping introduces negative charges and is called n-type doping. If Si is doped with B, Al or Ge (column III), the material contains free positively charged holes and the doping is called p-type.

Transistors consist of three adjacent regions - base, emitter and collector - in which the desired electrical properties are obtained by doping with impurity atoms. A bipolar transistor is essentially a switch. By applying the electrical charge to the base, the device can be turned "on" and an electrical current flows from the emitter to the collector, or "off" when the current is stopped. FET and MOSFET are the basic building blocks of a computer memory used to carry out logic operations. Both are made by setting three components: gate, source and drain, into a silicon substrate. When a negative voltage is applied to the p-channel, holes from the substrate are attracted and form a conductive channel under the SiO_2 insulating layer. When the voltage is removed the holes sink back into the bulk and the current is stopped.

3 ADVANCED SURFACES: HYPERFINE SURFACE STRUCTURES

Advanced surfaces provide opportunities to develop new surface materials and surface technology. Scientific interest in the properties of two-dimensional solids has led to the development of different types of surface materials. The recent development of hyperfine surface structures - clean surfaces, thin films and nanophase structures - opened up atomic/molecular studies of surface phenomena and new applications.

Surface science does not have such a long history as materials science. The birth of surface science can be traced to B. Franklin (18th century), who investigated the spontaneous spreading of oil on water. The use of surface chemical processes like catalysis (J. Dobereiner, G. Kirchof, J. Berzelius) began in the early years of the 19th century. The studies of tribology - friction, lubrication and adhesion - coincided with the industrial revolution when the use of moving parts became prevalent. However, some of this understanding appeared at the very beginning of the 16th century (Leonardo da Vinci). Thin, solid films were first obtained by electrolysis and chemical reactions. The existence of polyatomic or polymolecular aggregates, or colloids, was described by T. Graham in 1861. In 1866, H. Sorby found that the crystalline structure of a fractured surface depends on the chemical composition and the thermal treatment.

Interest in the physical processes of the surface started later. The first evaporated thin films and coatings were obtained in 1857 by M. Faraday, when he exploded metal wires in an inert atmosphere. Crooks discovered the possibility of the sputter-deposition of thin, metal films on glass using a glow-discharge tube. In 1903 A. Wehneld discovered that poorly emitted metal cathodes when coated with barium or other alkaline earth oxides produced a current a million times greater than uncoated metals. In 1914 I. Langmuir and W. Roger showed that tungsten wire containing a little thorium, which had been heat treated to diffuse a monolayer of thorium onto the surface, could emit a current 10^5 times higher than pure tungsten at the same temperature.

The properties of two-dimensional solids and the discontinuity between materials remained of academic interest until the development of vacuum equipment and equipment to control their properties. Clean surfaces have been studied since 1960 when economical ultra-high-vacuum (UHV) systems and new experimental techniques made possible the molecular and atomic-level investigation of surfaces. Consequently, macroscopic surface phenomena have been re-examined on the atomic and molecular level ⁹.

3.1 Clean surface

In the characterisation of solids, the most important area of interest is to define the state of the surface, a marked discontinuity from one material to another. At the beginning, surfaces were modelled as sharp discontinuities. Terrace's model (1950) revealed that the surface is rough. Depending on the energy of incoming particles or the chemical environment the surface atoms move and adjust their position in the bulk. The surface is flexible. Since no change in nature is ever instantaneous, there is a finite depth for any real surface and in characterisation we must consider what this depth is. In practice, the surface depth is defined by the choice of

characterisation method, it can be from one atomic layer to a few microns ¹⁰.

Surface materials can be divided into two groups: those that utilise their external surface and microporous materials where most of the surface resides in internal pores. The surface atom concentration may also vary depending on the crystal structure and the crystal face. The concentration of the atoms/molecules at the solid surface can be estimated from the bulk density. The bulk density of water/ice is 1 g/cm³, therefore the molecular density is 5 · 10²² mol/cm³. The surface concentration assuming cube-like packing $C = \rho^{2/3} \simeq 10^{15}$ mol/cm². Because the density of most solids is within a factor of 10 of each other, 10¹⁵ atoms/cm² is a good order-of-magnitude estimate for the surface concentration of atoms/molecules ¹¹.

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

$$F = \frac{N_A \cdot P}{2\pi MRT} \quad F(\text{at} / \text{cm}^2 / \text{s}) = \frac{3.5 \cdot 10^{22} \cdot P(\text{Torr})}{\sqrt{M(\text{g} / \text{mol})}}$$

where: M is the average molar mass of the gaseous species, T is the temperature in Kelvin, N_A is Avogadro's number and R is the gas constant. Using the value for a nitrogen molecule for which $M = 28$ g/mol, room temperature $T = 300$ K and Avogadro's number $N_A = 6,02 \cdot 10^{23}$ molecules/mol, we obtain $F = 10^{15}$ molecules /cm²/s. To keep the surface clean for 1s or 1h the flux of incident particles (atoms/molecules) must be less than 10¹⁵ or 10¹² particles/cm²/s, respectively. Under UHV conditions (1,33 · 10⁻⁷ Pa) it takes 10³ seconds before a surface is completely covered. If not, the surface on which atoms are deposited is always covered 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 (10⁻¹²s). The surface concentration σ at/cm² of adsorbed particles on a clean surface is given by:

$$\sigma = F\tau$$

where F is the incident flux.

For theoretical considerations, when the surface is covered with 10¹⁵ atoms/cm² we usually say that the surface is covered with a monoatomic layer. However, this is not the case. The atoms of the deposited layer are never distributed as a monoatomic layer. They diffuse and form a three-dimensional nucleus and clusters. A cluster grows and some atoms become surrounded by others and are no longer surface atoms. Particles of a finite size are described as a dispersion D (**Figure 1**).

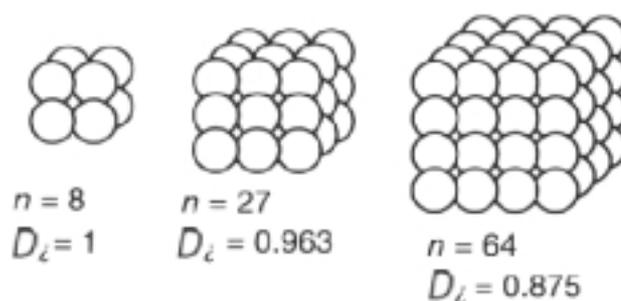


Figure 1: Number of atoms in the cluster (cubic crystal)

Slika 1: Število atomov v zgoščitvi (cluster) za kubični kristal

$D = N_s/N_{tot}$ (number of surface atoms/total number of atoms).

Only for a small nucleus is D equal to unity, while for a cluster D decreases with the number of atoms.

Finally, we must point out that the surface structure differs from the bulk substrate structure. Two phenomena occur at clean surfaces: relaxation and reconstruction ¹².

Relaxation. During the relaxation of metal surfaces the first layer of atoms moves inwards and this leads to a shortened interlayer spacing between the first and second layer of the surface (**Figure 2**). On rough surfaces, the atoms relax in order to smooth any irregularity. With ionic crystals, two ions move in such a way that the

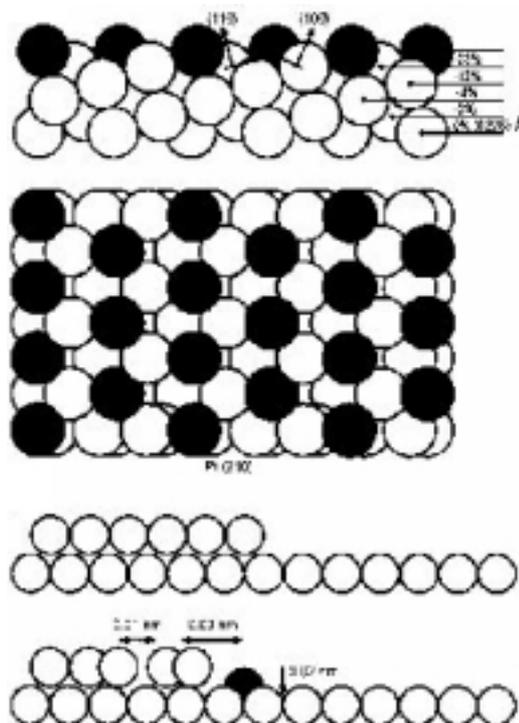


Figure 2: a) Relaxation at the clean crystal surface Pt (210), b) Restructuring at a step site; each atom attempts to optimise its coordination, "cracks" open on the step edges

Slika 2: a) Relaksacija čiste površine kristala Pt (210), b) rekonstrukcija na mestu stopnice; vsak atom želi optimizirati svojo koordinacijo, razpoke odprte na robovih stopnic

positive and negative ions are almost coplanar. Because of the necessary charge neutrality, this type of surface structure is more stable.

Reconstruction. The atoms at the surface move not only perpendicular but also in a parallel direction. This often leads to the formation of new unit cells. Such phenomena are called surface reconstruction ¹³. The surface structure of Pt, Au and Ir (100) that should have square unit cells reconstruct to form hexagonal surface unit cells.

Modification. When energetic particles strike a solid surface, many kinds of interactions take place. As a result of these interactions the following can occur: desorption; deposition of beam particles; the emission from solids and projectile implantation; and momentum transfer to the target atoms ¹⁴. All these processes are energy dependent and lead to a relocation of target atoms (**Figure 3**).

Low-energy beam interaction bridges the gap between chemical processes (chemisorption/adsorption, molecular beam, $E_0 < 5\text{eV}$) and physical processes (sputtering, implantation, mixing, $E_0 > 50\text{-}100\text{ eV}$). Chemical sputtering with small energies is observed when the impinging particles react with the target atoms to produce a volatile chemical compound.

Physical sputtering occurs at incident energies of a few hundred eV and higher ¹⁰. Of particular interest are the three regions in which species react or are trapped by the surface ¹⁵. The zones are described by sticking coefficient or reaction probabilities P (the number of deposited atoms/number of impinging reactant atoms).

Low-energy beams, with an incident energy E_k of a few tens of 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,
2. The reaction product or deposit is not volatile.

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. The penetration depth of the

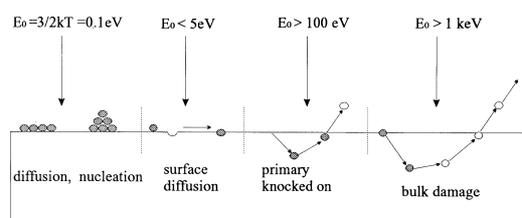


Figure 3: Simplified comparison of the incident particle path for: a and b) for a low-energy beam, c) for a medium-energy beam and d) for a high-energy beam-activated reaction

Slika 3: Poenostavljena primerjava vpadnega delca za: a) in b) snop z majhno energijo, c) snop s srednjo energijo in d) snop z reakcijo, ki jo sproži snop z veliko energijo

beam particles into the material allows the materials to be modified according to requirements. Depending on the incident-beam parameters and the target, it is possible to characterise a few collision events: linear collision cascade and spike-regime.

Surface-modification techniques have been applied mostly in semiconductor technology. The implantation of yttrium into the near-surface region improves the mechanical properties and the resistance to oxidation of stainless steel and the implantation of N_2 reduces the coefficient of friction and increases the hardness of the surface. Ion-beam processing can alter the biomaterial characteristics of, for example, surgical implants.

3.2 Thin Films

Thin-film studies have advanced many new areas of research. A number of methods have been developed - physical and chemical vapour deposition, electroplating and spraying - to prepare thin films/coatings of different types of material. The criteria for selecting a deposition process and a material depend on the actual applications. The properties of the deposit depend on the starting material, the method used, the vacuum, the deposition condition, the properties of the substrate and the final thickness. The fundamental relationships between processing parameters and microstructure, as well as between microstructure and the thin-film/coating properties are important to determine the system's quality.

Physical and chemical vapour deposition are the most commonly used methods for the deposition of different types and structures of thin films. Since the gaseous materials that are evaporated and sputtered are very sensitive to the presence of impurities it is necessary to work under high-vacuum conditions to obtain high-quality thin films/coatings.

The deposition of thin films/coatings in a vacuum consists of several steps:

- Transition of the solid or liquid phase to the gaseous phase; the evaporation rate N_e from a clean surface of unit area in a vacuum is given by the Langmuire expression:

$$N_e = 3.513 \cdot 10^{22} p_e \sqrt{1/MT}$$

where p_e is the pressure in Torr, T is the temperature in $^\circ\text{C}$ and M is the molecular weight,

- Transport of gaseous material from the vapour source to the substrate at a low enough pressure; the mean free path of all gas particles is inversely proportional to the gas pressure:

$$\lambda = \frac{V}{N} \frac{1}{\pi d^2 \sqrt{2}} = \frac{kT}{p_e \pi d^2 \sqrt{2}}$$

where, d is the molecular diameter and p_e is substituted for N/V ,

- Condensation of the vapour phase on the appropriated substrate; the probability that an atom

will be incorporated into the surface is the "condensation" or "sticking" coefficient; the degree of thermal equilibrium is described by the thermal accommodation coefficient:

$$\alpha_T = \frac{E_v - E_r}{E_v - E_s} = \frac{T_v - T_r}{T_v - T_s}$$

where: E_v is the incident energy of the vapour atoms; E_r is the energy of the desorbed atoms before equilibration with the substrate; E_s is the energy of the desorbed atoms after equilibration with the substrate and T_v , T_r and T_s are the corresponding temperatures.

The first characterisation of a thin film's structural characteristics includes an analysis of homogeneity as a function of thickness of the deposited material ¹⁶. Four stages characterising the distribution of the condensed material are evident. The first stage (up to 10 nm for Au) consists of three-dimensional islands, the crystallographic shapes of which depend on the deposition conditions and the surface energy of the substrate. The growth is controlled by diffusion. After further deposition the islands grow, the nuclei coalesce and empty channels (width 5-20 nm) that are randomly distributed on the substrate are formed. In the case of Au, for a thickness greater than 30 nm (for other materials it depends on T_m), a thin film is continuously deposited on the substrate. Microstructure, sizes, shapes and orientation of the crystal grains and morphology of the surface material are strictly thin-film phenomena, which depend on deposition parameters and substrate properties (**Figure 4**).

Depending on the physical and chemical properties of the substrate and the deposition parameters, various

types of growth can occur: island growth (Volmer-Weber mechanism), when the condensing material is more strongly bonded to itself than to the substrate; layer growth (Frank-Van der Merwe), the opposite situation; and island-layer growth (Stranski-Krastanov), when some layers are required before the memory of the substrate is lost.

The microstructure of the coatings may vary from defect-free single crystals (on a single-crystal substrate) to highly columnar and faceted structures. The resulting structure depends on how the atoms are incorporated into the existing substrate structure.

The large variety of deposited thin films/coatings that can be grown by the PVD (Physical Vapour Deposition) technique have a 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 major application of thin-film components is in integrated thin-film networks. Circuits consisting of thin-film resistors (NiCr), capacitors (Ta_2O_5), contacts (Al, TiPdAu), and interconnections are produced for different purposes. Integrated circuits can simply be described as a thin block of semiconductor, usually Si, which contains precisely doped regions on the surface and geometrically patterned thin films of metals and insulators.

Over the last 50 years interest in the mechanical properties of thin films/coatings and the possibility of

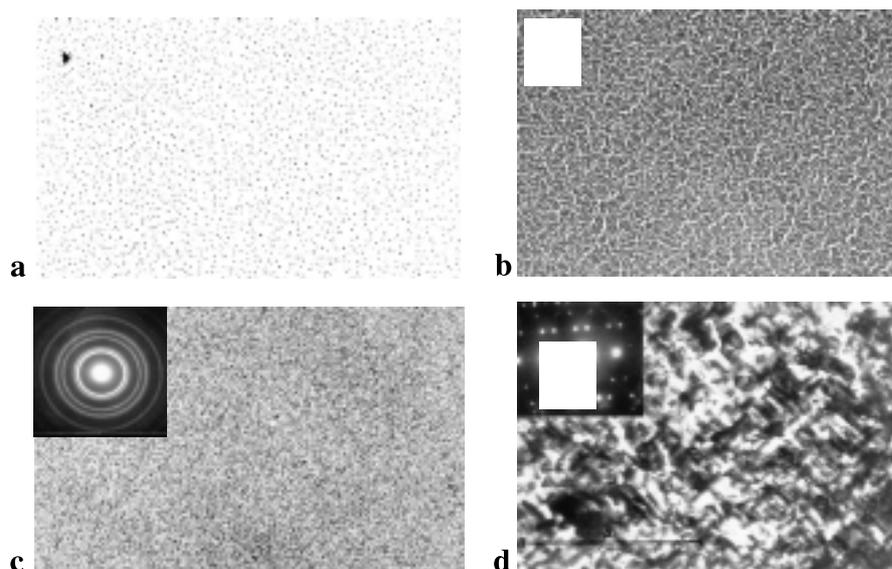


Figure 4: Steps of the thin-film/coating growth presented schematically: a) formation and coalescence of islands, b) the large islands growth, c) the channels and holes, d) continuous film/coating

Slika 4: Shematičen prikaz stopenj pri rasti tanke plasti: a) nastanek in koalescenca otočkov, b) rast velikih otočkov, c) kanali in luknje, d) zvezna plast

their application has been growing. The most frequently investigated mechanical properties of thin films/coatings are their adhesion to substrates, mechanical stresses and their tensile properties. The largest class of hard coatings can be found among transition-metal nitrides, borides and carbides. A number of ceramic coatings have been deposited using CVD processes. The oxide coatings of Al_2O_3 are mostly used as protection against chemical corrosion or as electrical insulators. The most studied nitride coating is TiN, which exhibits a large variation in properties as we go across the homogeneity range. Carbide coatings have, in general, a higher hardness than TiN, but the growth of carbides is more complicated. A high-strength material could be obtained by the deposition of a layered structure of two materials (TiN/NbN).

3.3. Nanophase structures

The properties of a material are not determined only by the chemical composition, alloying, cold working, annealing or deposition methods. When certain metals are processed in such a way that their grain size is smaller than $10\ \mu\text{m}$ their structure is stronger and more stable.

An ordered array of atoms and idealised structures cannot explain all the observed material properties. Unique properties are based on a deviation from the ideal crystal structure. It was found that defects in the space lattice and deviations from the exact periodicity of the crystal - stacking faults, grain boundaries and dislocations - play a dominant role in determining the mechanical properties and high-temperature behaviour. Defects are considered in terms of their geometry: zero-dimensional or point defects (vacancy and interstitial); one-dimensional or line defects (dislocations); two-dimensional or surface defects (grain boundary and twin boundary); and three-dimensional or volume defects (voids, porosity and inclusions).

Theories have been developed to explain the role of defects in material properties and the performance of working components. In turn, it was also possible to manipulate defects to obtain desired structures and properties.

When a material is a mixture of a few components, it may exist with two or three phases. The phases are in equilibrium - minimum energy state for a given temperature, pressure and composition - under idealised conditions. By processing materials, a new atomic or structural configuration can be obtained. Consequently, the structure and properties can be altered.

Advanced techniques for processing materials enable us to shape and form samples and to exploit microstructural knowledge. Fine grain sizes of less than $10\ \mu\text{m}$ to few nm are produced by many methods: superplastic forming (from pre-alloyed 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. It was found that a fine grain size, the presence of a crystal of second phase or a repetitive structure of the deposited thin films improve a material's properties. The interface between individual grains, different phases or deposited layers, acts as a barrier to the motion of dislocations and is mainly responsible for the plastic deformation of crystalline solids. Fine-grained material is harder and stronger because the surface/interface atoms are not bonded to the maximum number of neighbours and are in a higher energy state than the 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 the applied stress, k and d are constants for a particular material.

The need for more efficient uses of materials invites a close look at the nanophase structure of materials. Nanoparticles represent surfaces in three dimensions and studies of their properties are important for new surface materials. The explosion of scientific and industrial interest in these materials in the last decade arises from their properties.

Nanostructured materials may be defined as materials whose structural elements have dimensions in the range from $1\ \text{nm}$ to $100\ \text{nm}$ ¹⁷. A nanocrystal is a fragment comprising between a few and a few tens of atoms. Cluster synthesis can be done by the following methods: gas-phase synthesis (clusters are formed in the gas phase and then 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 some of the following areas: the development of techniques for obtaining nanoclusters of various compositions, the passivation of the cluster surface and the assembly of nanoclusters into well-ordered nanostructured solids. (Carbon-based nanostructures and fluorine C_{60} require a separate discussion¹⁸). The resulting nanostructures must be able to withstand thermal fatigue, aerodynamic loads, corrosive gases and other extreme working conditions.

The properties of nanophase materials depend not only on crystal size, but also on crystal surfaces and grain-boundary characteristics. In this region dislocations change the direction of motion and the slip planes must overcome this discontinuity. It has been suggested that a high-strength material could be obtained by the deposition of a layered structure of two materials with the same crystal structure¹⁹. Soon after, by the deposition of two thin films TiN/NbN with nanometer thickness, a superlattice structure with high hardness was obtained. Superhard superlattices are characterized by a

bilayer repeat period λ , the distance between each successive pair of deposited material (**Figure 5**).

The critical stress σ_c required to move a dislocation across an interface is given by:

$$\sigma_c = (E_A - E_B)/(E_A + E_B).$$

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

A superhard superlattice of TiN/NbN makes the material scientifically and technologically very interesting. The hardness of TiN/NbN with $\lambda = 4,6$ nm is almost equal to the highest hardness of cubic BN (50 GPa). The structure of deposited TiN/NbN is easily produced by sputtering. The interfaces between the deposited material can act as energy barriers to the motion of dislocations.

The 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 temperatures. Its low coefficient of thermal expansion limits its use in the cutting of iron-based materials. Synthesising cubic BN is difficult. New methods and techniques developed by three-dimensional surface science provide opportunities to replace natural materials with man-made materials.

Because of a high two-dimensional defect concentration, the density of nanophase materials is lower than the density of crystalline materials. Comparing with crystalline material of the same composition, nanophase structures have a 10-25% lower density. The crystallites of nanophase materials have a 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 $V_m = MV/m$.

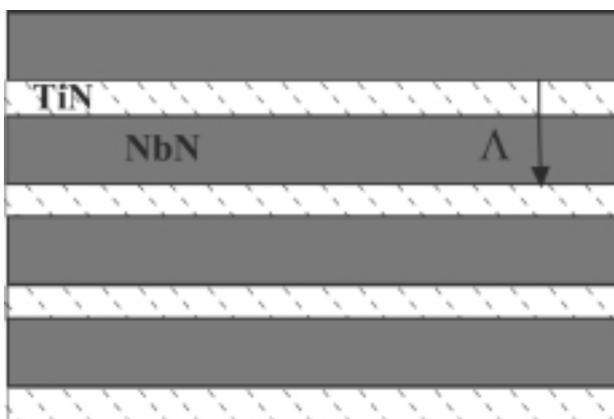


Figure 5: Cross-section through a single-crystal superhard superlattice TiN/NbN with a bilayer repeat period $\lambda = 5$ nm

Slika 5: Prezrez skozi nanokristalno supertrdo supermrežo TiN/NbN s periodo 5 nm

4 CHARACTERIZATION OF SOLID SURFACES

The main domains of energetic beam-surface interactions are the implementation of materials and materials analysis. The most modern characterisation techniques for structural and compositional analyses are scattering techniques. The incident medium- or low-energy beam - electrons, photons or ions - interacts with the solid sample and gives rise to scattered beams, which can also be in the form of electrons, photons or charged particles (**Table 2**).

Table 2: Scattering technique for structural and compositional analyses

Inc. beam	Scattered or emitted beam			
	Electrons	Photons	Ions	X ray
Electrons	TEM, SEM, STEM, LEED, HEED, HRAES	Cathode luminescence		
Photons	Photo-emission	Optical microscopy		
Ions	Secondary electron emission	Ion - ind. photons	RBS, NRA, SIMS	
X - ray	XPS			Diffraction, fluoresc.

By analysing the scattered beams, structural and compositional information about the samples can be obtained²⁰. Since many of the beam-induced scattering techniques are complementary, it is recommended to use more than one in characterising a sample.

In the last decade, material characterisation has been moving in the direction of microanalysis: the analysis of the structure and composition of a very small volume of a material. One basic requirement of microanalysis is to have a high lateral resolution of the order of atomic dimensions. This is not available in most techniques for surface and thin-film characterisation. In fact, characterisation techniques often sacrifice their lateral resolution to gain in-depth resolution. To improve the lateral resolution in scattering-based techniques the size of the primary beam must be reduced: by the use of a smaller beam source and by beam focusing onto a spot as small as 5 Å for the electrons. With such an electron beam it would be possible to get information about a very small volume (10^7 Å³) and at the same time to image a large area of the sample by scanning the beam. The new techniques for microanalysis - field ion microscopy and the scanning-tunnelling microscope - can provide information about the surface structure at the atomic level (**Figure 6**).

The assumption in many physical methods of characterisation is that the incident beam does not disturb the crystal structure and the distribution of elements in the solid that is being analysed. For almost all the methods that use particle or radiation beams this is not the case.

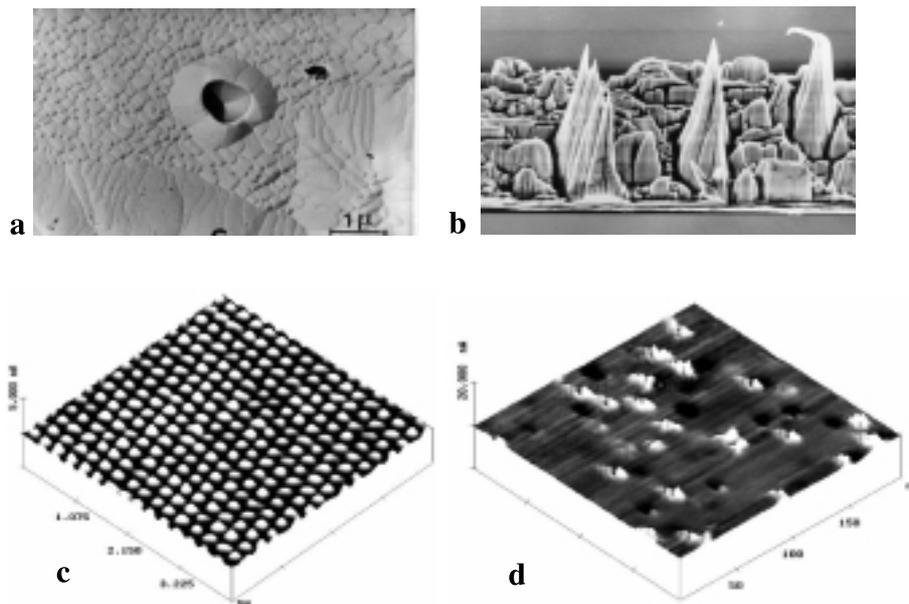


Figure 6: Topography of: a) bombarded uranium (TEM replica), b) Cu/Ag alloy (SEM); c) and d) chromium clusters deposited on HOPG (STM)
Slika 6: Topologija: a) obsevani uran (TEM-replika), b) zlitina Cu/Ag (SEM) in c) klastri kroma, naneseeni na HOPG (SEM)

Along the path of the radiation in solids, the electron beam alters the mechanical properties, the neutron beam alters the electrical and magnetic properties, the ion beam alters the thermal and surface properties as well as chemical activities, and finally, uncharged laser beams cause local heating and diffusion in solids²¹. Depending on the energy of the incident species and the target properties, the bombardment surface region may consist of several overlapping interacting layers.

5 CONCLUSION

The results obtained relating to advanced materials are the basis of research into smart structures and intelligent material systems. No results have been published yet on smart and intelligent material structures - which are limited to nature - although some components of such a system have been demonstrated. Magnetostrictive materials and some molecular ferromagnets change their dimensions in magnetic fields; shape-memory alloys (NiTi) act as actuators by having a phase transition at a specific temperature and reversing then to their original shape; piezoelectric ceramics can act as sensors depending on their polarity; biopolymers contract and expand in response to temperature or chemical changes in the environment. A complete smart-material system would contain: sensors, actuators, signal processors, communication network and energy source. Many technological problems need to be overcome before such applications reach the market.

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