

ELECTROCHEMICAL NANOSTRUCTURING

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Summary

Over the last two decades, electrochemical nanostructuring has become a very attractive and cost-effective approach for tailoring the properties of Si, III-V and II-VI semiconductors. Conductive matrices with quasi-ordered or ordered distribution of nanochannels and structures with very large surface and aspect ratios were developed for various applications. The authors show that electrochemically produced arrays of nanochannels induce artificial birefringence, enhanced optical second harmonic generation and Terahertz emission, enables one to modify the optical phonon spectrum in a controlled fashion, to produce waveguiding, random lasing structures etc. Two-dimensional metallo-dielectric structures with spectacular properties were fabricated by electrodeposition of thin metal films on inner surface of pores, this approach opening new opportunities for the development of novel nanomaterials and device structures on their basis.

1. What is Electrochemical Nanostructuring?

There are two main approaches for structuring – bottom-up and top-down. A bottom-up structuring process starts with a substrate and a gradual deposition of different layers leads finally to a structured material. A top-down structuring, on the other hand, removes gradually, i.e. etches, material from the substrate. Thus, surface or bulk modification of an object by adding or removing material is called structuring.

For a better control over the final structure the bottom-up as well as top-down approaches in practice are usually combined with lithography techniques. A schematic representation of the two approaches is illustrated in Figure 1.

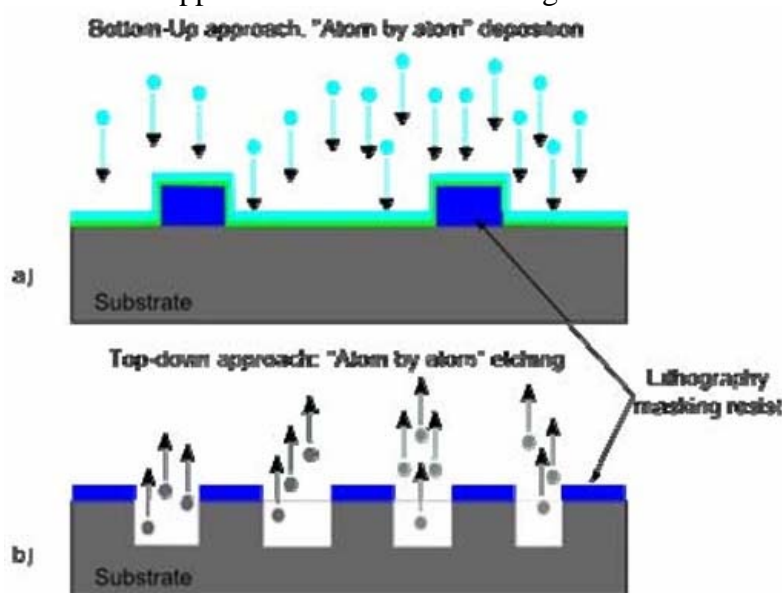


Figure 1. a) Bottom-up approach; b) Top-Down approach. Lithography masking resist is used in order to protect certain regions on the substrate against deposition or etching respectively.

An electrochemical process is a chemical process taking place usually at the interface between a solution and a solid as a result of an electrical current flow through this interface. Top-down as well as bottom-up approaches for structuring can be realized by means of electrochemical processes.

Thus, electrochemical nanostructuring is a way of modifying the surface or bulk of a material by passing an electrical current between the material and a solution, so that the resulting object has components with dimensions on the nanometer scale.

2. Basic Principles of Electrochemistry

2.1. Solids

A solid is a collection of 10^{22} cm^{-3} interacting atoms. When the atoms are brought in a solid close enough to each other, the atomic energy levels split into bands. According to the so called “band theory” an atomic level will generate $\sim 2 \cdot 10^{22} \text{ cm}^{-3}$ different energy

levels in a band. A schematic splitting of atomic levels in a solid is presented in Figure 2.

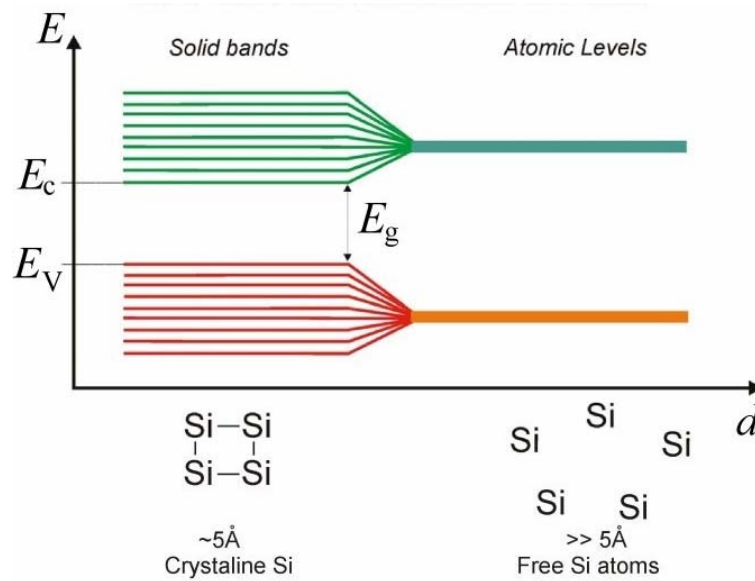


Figure 2. A schematic representation of splitting of atomic energy levels into bands by decreasing the distance between the atoms up to several Angstroms.

Two atomic levels are of considerable importance: the last occupied and the first unoccupied by electrons. Consequently they generate two energetic bands in a solid: the so called valence band (E_V) and conductance band (E_C) respectively. E_V - band is usually completely occupied by electrons, whereas the E_C - band will be partially or totally free of electrons. The distance between E_V and E_C is called electronic band gap (E_g). Metallic, semiconductor or dielectric properties of a solid are determined by how the two bands are positioned relative to each other.

In metals the valence and conduction bands 1) do not overlap, but E_C - band is partially filled with electrons ($T = 0$ K), or 2) the E_V and E_C -bands overlap (Figure 3a).

For semiconductors E_V and E_C - bands do not overlap. E_C -band is free, whereas E_V - band is completely filled with electrons ($T = 0$ K). E_g in semiconductors is usually smaller than 3 eV (Figure 3b).

Dielectrics are similar to semiconductors, however with $E_g \gg 3\text{eV}$ (Figure 3c).

The movement of electrons in a solid defines its electrical conductivity. An electron can move only if free energy levels are available in its band. Metals have a partially filled E_C -band, therefore the electrons can move freely and the conductivity of metals is very high.

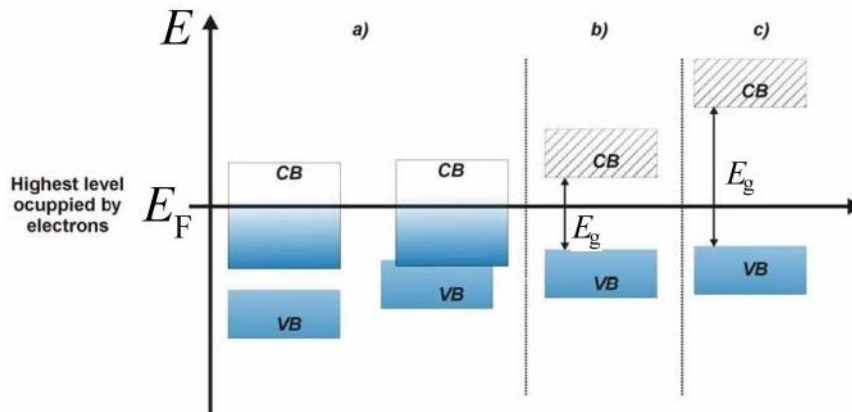


Figure 3. A schematic band occupation by electron in metals, semiconductors and dielectrics.

For insulators no free energy levels are present in E_V -band. More than that E_g is large and the electrons can not “jump” from E_V -band to E_C -band where plenty of free energy levels are available. Therefore, the conductivity of insulators is nearly zero.

In semiconductors E_g is not too large and the electrons can “jump” into the E_C -band and move freely there. However, the number of such electrons is lower than in metals therefore their conductivity is also lower. An interesting fact about semiconductors is that “jumping” of electrons into the E_C -band generates positively charged vacancies (the so called “holes”) into E_V -band. Therefore, when talking about semiconductors two types of charge carriers are considered: electrons in E_C -band and holes in E_V -band.

The electrons can be transferred into E_C -band electrically, thermally or optically. However, there is another method for generating mobile charge carriers in semiconductors referred as doping. Doping involves the addition of tiny amounts of a different chemical element into the semiconductor. The simplest example is the introduction of a group V element (donor, *e.g.*, Phosphor, P) or a group III element (acceptor, *e.g.*, Boron, B) into a group IV crystal (host, *e.g.*, Silicon, Si).

The addition of P into Si introduces occupied energy levels into the band gap close to E_C , thereby allowing an easy transfer of electrons from the P-atoms into the E_C -band of Si. On the other hand, *e.g.* the addition of B introduces vacant energy levels into the band gap close to E_V , which facilitates the transfer of electrons from E_V to B-atoms.

Doped semiconductors where the dominant charge carriers are electrons are called n-type, whereas those where the majority charge carriers are holes are called p-type semiconductors (Figure 4). Undoped semiconductors are called intrinsic.

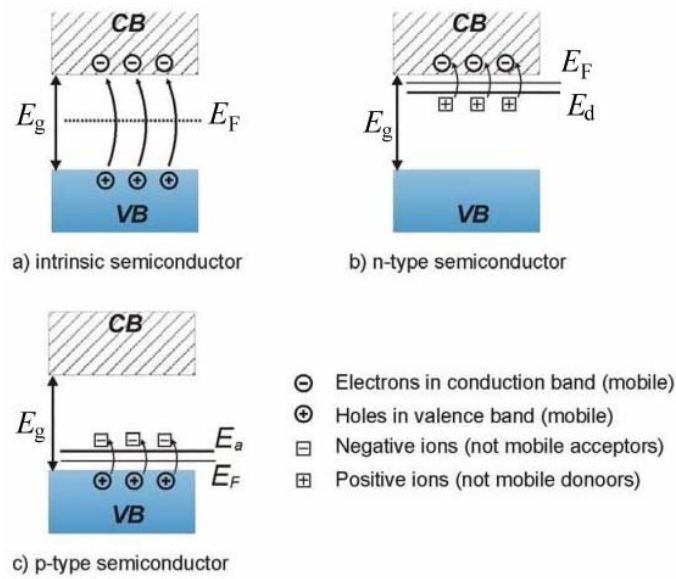


Figure 4. The three types of semiconductors: a) Intrinsic semiconductors. b) n-type semiconductors. c) p-type semiconductors.

A very important concept used to describe the thermo-dynamical equilibrium of charges in solid state materials is the Fermi level (E_F). E_F is defined as the energy level where the probability of occupation by an electron is equal to 1/2. For metals at $T = 0\text{ K}$ the Fermi level represents the energy level separating the occupied from unoccupied by electrons levels. In semiconductors the occupied and unoccupied levels are separated by E_g and therefore for an undoped semiconductor E_F level lies at the mid point of E_g (Figure 4a). For n-type semiconductors the E_F lies just below E_C (Figure 4b), whereas for p-type lies just above E_V (Figure 4c).

2.2. Electrolytes

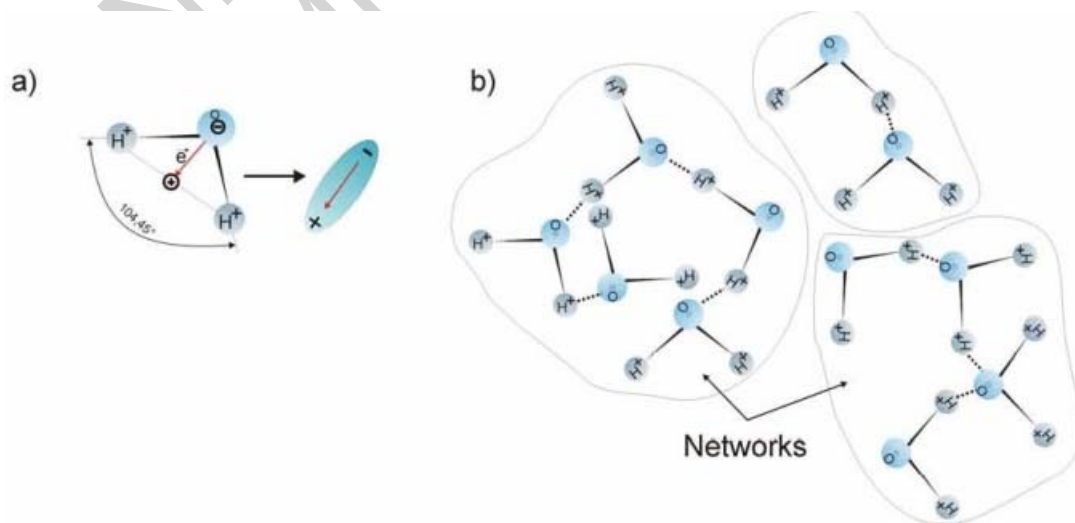


Figure 5a). Water as an electric dipole; b) Water in its liquid state.

Water (H_2O) is one of the main components of nearly any electrolyte solution. The electrons of the oxygen atom interact with the electrons of the hydrogen atom and form covalent bonds. The angle between the covalent O-H bonds is $\sim 104.45^\circ$ (Figure 5a). Due to this spatial bond distribution the molecules of water behave like an electrical dipole.

Besides the two covalent bonds a water molecule has also “unused” electronic orbitals, which can be utilized to form bonds with other H-atoms from neighboring H_2O -molecules. The structure of water in its liquid form is more or less an agglomeration of water networks, as depicted in Figure 5b.

Besides water, an electrolyte contains also ions. Due to the electrical field of each ion, the H_2O -dipoles surrounding it will reorient along this field. These water molecules form the 1st-solvation level of an ion and move together with the ion through the solution (Figure 6). Outside the 1st-solvation layer water dipoles will become less oriented and form the 2nd-solvation level. At even larger distances from the ion the water regains its normal structure.

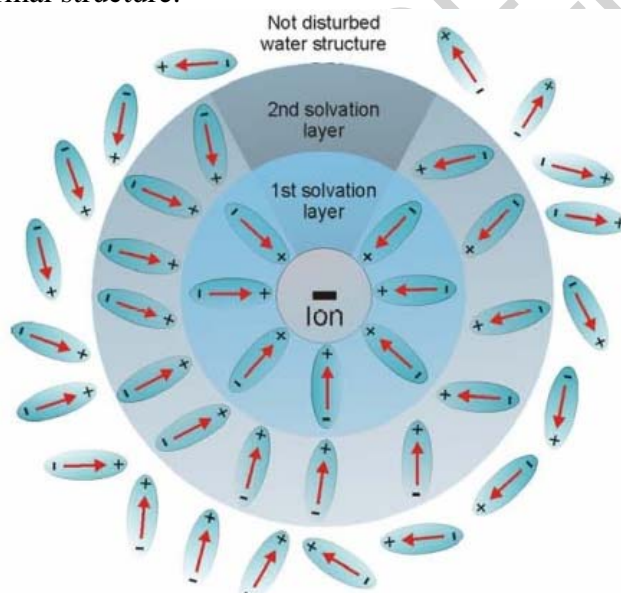


Figure 6. A schematic representation of ion solvation layers in electrolyte solutions

The presence of ions in water transforms it in an ionic conductor. Taking into account that electrochemistry is dealing with ionic as well as electronic conductors it is advisable to use for description of electrolytes the “band theory” formalism as for solids.

The “band theory” model for solutions is more complicated compared to that described above for solids. The reason is that the polar solvent and its thermal fluctuations affect the potential distribution of that ion. Due to this, the energy level of the ion will fluctuate as well and therefore the energy levels of ions in solutions must be described in terms of probability distributions.

The energy levels (oxidation states) of an ion in solution reflects the tendency of that ion to release electrons (reducing species, E_{red}) or to accept electrons (oxidizing species, E_{ox}) when the ion approaches an electronic conductor or another ion. Pairs of reducing and oxidizing species are called redox couples. In Figure 7 Gauss functions centered at E_{ox} and E_{red} are sketched, which represent the probability distribution of the fluctuating energy levels of an ion in solution.

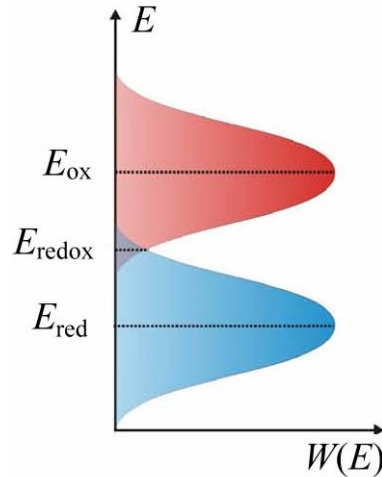


Figure 7. Fluctuating energy levels in a polar solution.

The energy splitting between E_{ox} and E_{red} can be explained as follows. E_{red} -level belongs to an ion which tends to donate an electron. After the electron transfer took place, the resulted ion has a lower positive charge and the solvation shell will relax to a new equilibrium distribution (E_{ox}). Thus, the interaction of the ion with the solvent effectively splits the electron energy levels of the oxidized and reduced species (Figure 7).

For a solution containing one dominant redox couple it is convenient to define an "effective Fermi level" E_{redox} , which is defined so that at equilibrium between a solution and a solid the following relation is satisfied:

$$E_{\text{redox}}(\text{solution}) = E_{\text{F}}(\text{solid}) \quad (1)$$

where E_{F} is the Fermi energy in the solid.

Of particular interest is the redox energy level of a redox couple when an equal number of reducing and oxidizing species in the solution are present (E_{redox}°). Nernst equation gives the relation between E_{redox}° and E_{redox} .

$$E_{\text{redox}} = E_{\text{redox}}^{\circ} - kT \times \ln \left(\frac{[E_{\text{ox}}]}{[E_{\text{red}}]} \right) \quad (2)$$

where $[E_{\text{ox}}]$ and $[E_{\text{red}}]$ are the concentrations of the oxidizing and reducing species respectively, k is the so called Boltzmann constant and T is the temperature. It is also possible to demonstrate that:

$$E_{\text{redox}}^{\circ} = \frac{1}{2} \times (E_{\text{ox}} + E_{\text{red}}) \quad (3)$$

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Biographical Sketches

Sergiu Langa graduated from the Technical University of Moldova and received his PhD in materials science from the Christian-Albrechts University, Kiel, Germany. He held various positions at Infineon and Qimonda, dealing with the development and production of DRAM-memory chips, and at the Fraunhofer Institute for Photonic Microsystems in Dresden, Germany. The main scientific work is in the field of porous structures in III-V semiconductors obtained by electrochemical etching, and their application in micro-and optoelectronics.

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