SYNTHESIS OF NANOPHASES

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Contents

Summary

The principal modern methods used in the synthesis of nanophases are described. First the growth of quantum wells, using molecular beam epitaxy or metal organic chemical vapor deposition, is considered. Some of the methods determining the self-assembly of quantum wires on epitaxial substrates are then presented, and their relevance to nanofabrication discussed. Finally, the synthesis of quantum dots through colloidal chemistry, and hetero-epitaxial growth on mismatched surfaces, are both considered.

1. Structure and Properties of Nanophases

The degree of control achievable over the structure, defect density, and optical and electronic properties of synthesized materials has increased tremendously in recent years. This is strongly related to the development of advanced growth techniques, such as molecular beam epitaxy (MBE), and of the capability to investigate surface structures with atomic resolution, which was first attained with scanning tunneling microscopy (STM). Thanks to these techniques, it is now possible to grow solid systems with characteristic dimensions that may be in the order of the nanometer. At the extreme, it is

possible to build circuits whose smallest working parts are composed of between a thousand and a million atoms. In these cases it is more appropriate to treat this part of the device as a large molecule, rather than as a small solid particle. These structures are usually referred to as *nanostructures*, *nanocrystals*, or *nanophases*.

The peculiar properties of nanostructures are determined by two main features: the high ratio between surface and volume, and the occurrence of quantum effects due to the limited space available to electrons to move in the direction of the nanometer-range dimension. The increased surface-to-volume ratio determines a change in the free energy of the solid that affects properties such as the melting and solid–solid phase transition temperatures. What appears most striking in nanostructures, however, is the change in electronic and optical properties. This can be exploited, for example, in building extremely small and efficient lasers, solar cells, or transistors.

Nanostructures can be obtained by confining the extension of a crystalline material in one, two, or three dimensions. The first nanostructures produced were confined in one direction, and consisted of a thin epitaxial film of GaAs sandwiched between an upper and a lower layer of a higher-band gap semiconductor. This compound was $Al_{0.3}Ga_{0.7}As$; the subscripts 0.3 and 0.7 indicate that for each 10 As atoms (that belong to the VA group of the elements) three atoms of Al and seven of Ga (both belonging to the IIIA group of the elements) are present. The alloying of GaAs with Al increases the energy required to move the electrons from the valence to the conduction band from 1.42 eV to 2.0 eV at the limits of a very small change in its lattice constant. (The lattice constant of GaAs is 5.653 Å, and that of AlAs is 5.662 Å). This latter feature is extremely important since it allows very smooth and defect-free interfaces between the two semiconductors. Because of the higher band gap of $Al_{0.3}Ga_{0.7}As$, the mobility of the electrons perpendicular to the GaAs plane is limited to a dimension equal to the GaAs thickness. In the GaAs layer the electrons are free to move in two dimensions. If the GaAs layer is sufficiently thin (in other words, thinner than the De Broglie wavelength, about 300 Å in this case) this leads to quantization of the energy that the electrons can transmit in the confined direction. The electronic energy becomes dependent on the thickness *d* of the quantum well, according to the following equation (see *Schröedinger Equation and Quantum Chemistry*):

$$E_n = E_0 + \frac{\hbar^2 n^2}{2m_e d_{QW}^2} \qquad (1)$$

where n is an integer and m_e is the mass of the electron. This situation is identical to that of an ideal quantum particle confined in a box, and therefore the structures determining this behavior were named *quantum wells*. Electrons can also be confined in two and three dimensions, and accordingly the corresponding structures are named *quantum wires* and *quantum dots*. A sketch of the density of states reported as a function of the energy of the bulk semiconductor and different nanostructures is shown in Figure 1.

The intensity of research interest in the growth of nanostructures is due to their exceptional properties. In particular, the quantization of the energy levels, the absence of dopants, and the ability of the confined layer (well, wire, or dot) to obtain electrons

from the surrounding barrier layers allow high current densities to be attained. Therefore, it is possible to build very fast transistors and (because of the formation of excitons—the systems constituted by an electron and a hole) highly efficient and powerful lasers. Progress in the field of quantum well lasers has been such that they are nowadays used industrially in the latest generation of compact disk players. Quantum wires and dots, in contrast, are still far from any technological application, mainly because of the problems connected with the synthesis of these systems, and the difficulty of building a device that can have a significant lifespan at room temperature.

In the following section, the main methods nowadays adopted for growing nanostructures will be described, considering first the techniques used to build quantum wells, and then those adopted for quantum wires and quantum dots.

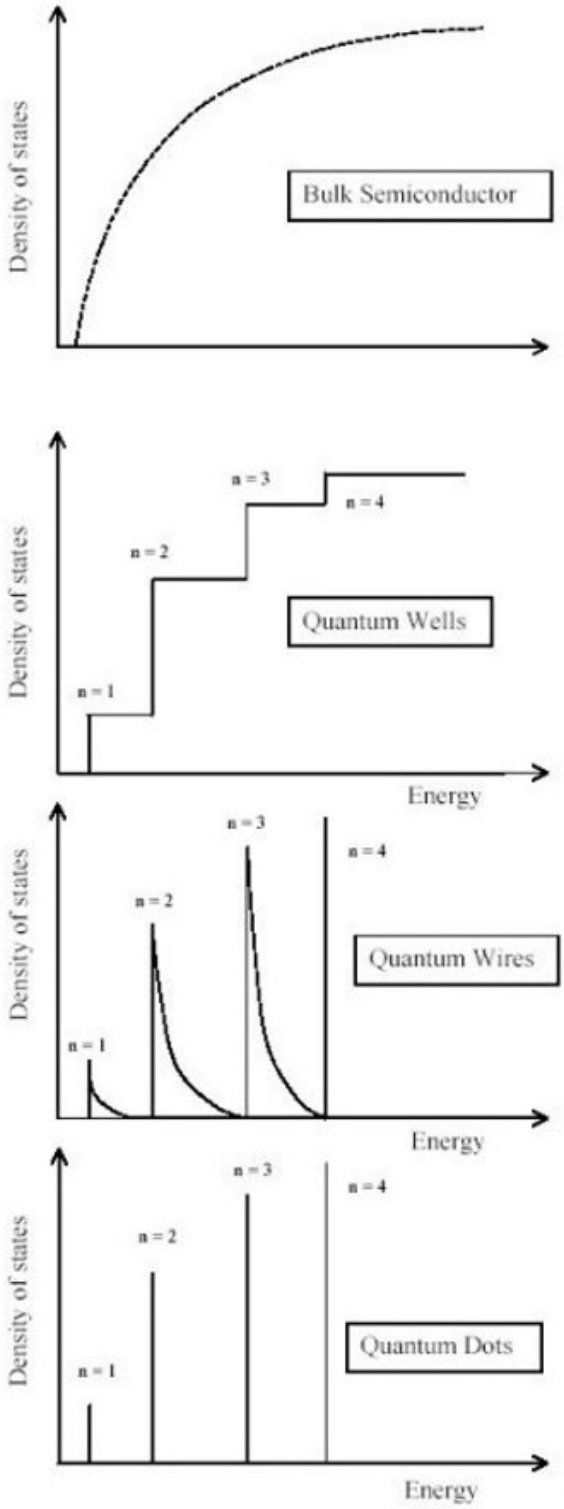

Figure 1. Density of states of different nanostructures compared with that of a bulk semiconductor, where n is the integer appearing in Eq. (1)

2. Synthesis of Quantum Wells

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Biographical Sketch

Carlo Cavallotti was born in Milano, Italy, on July 17, 1971. He graduated in chemical engineering in 1995 at Politecnico di Milano and took a Ph.D. in chemical engineering in 1999 at Politecnico di Milano. During the Ph.D. he spent a six-month period as visiting student at the Massachusetts Institute of Technology. Since 1999 he has worked as a researcher at the Department of Applied Physical Chemistry,

Politecnico di Milano. In 2000, he won the XII National Award "Federchimica—per un futuro intelligente," reserved for chemical researchers and professors. His research interests include the synthesis of advanced materials through chemical vapor deposition, the realization of models capable of describing phenomena occurring on different length scales, and the study of surface chemistry through *ab initio* methods and statistical thermodynamics. He is the author of about twenty articles, mainly published in international journals.