

BOOK REVIEW

Cluster beam synthesis of nanostructured materials. P. Milani, S. Iannotta, 1999, In: Springer series in cluster physics; Springer, Berlin, Heidelberg, New York. Printed pages 190; price: DM 129.00. ISBN 3-540-64370-2

Clusters are assemblies of atoms ranging in size from only a few up to several thousands of atoms. They have been routinely produced in molecular beams during the past 20 years to study their intrinsic properties, which vary from atomic to bulk-like behavior. These studies of the free particles revealed that their physical and chemical properties are strongly size dependent. This gives them a great potential for basic investigations and possible applications where a tuning of properties is necessary on a very fine scale, e.g. in catalysis and microelectronics. However, to make use of their unusual properties they have to be synthesized and isolated either in bulk quantities or as films and nanostructures on surfaces. With a few exceptions (e.g. fullerenes and related materials), bulk synthesis of the pure clusters, i.e. ligand free, has not been achieved yet, but cluster deposition on surfaces is beginning to emerge in research laboratories around the world as a possible pathway to produce at least microscopic quantities of these exceptional materials.

The present book aims to introduce the last-mentioned topic to a broad readership not yet familiar with the possible prospects of the field. Since there are only a limited number of experimental results available in this area up to now, the authors put great weight on the introduction and discussion of available and possible experimental techniques. After a short prologue (chapter 1), the book starts with the description of molecular beams and the cluster formation process (chapter 2). Effusive and supersonic beams are described and the fundamental theory in terms of classical nucleation theory and condensation in molecular beams is presented. The semi-empirical approach might be especially helpful to understand the nucleation in cluster beams, since most of the experimental work on cluster production still relies on empirical data.

A detailed description of the experimental techniques used for cluster production is given in chapter 3. Since most of the materials which are of potential interest at the moment have a low vapor pressure under standard conditions, one has to employ several vaporization methods, which range from simple Joule heating to the erosion by particles and photons. The vapor generated in this way is embedded either in a continuous or a pulsed flow of seed gas (e.g. rare gases) to thermalize the material and to form the desired cluster beam. Special emphasis is put on continuous gas aggregation and supersonic sources and on pulsed laser vaporization and electrical discharge sources. These methods are discussed with emphasis on the maximum cluster intensity achievable with respect to cluster deposition.

Chapter 4 describes how the previously generated cluster beams can be characterized and manipulated. The basics and the technical setup of the mass spectrometers (MS) commonly employed in cluster research are explained in detail, i.e. quadrupole MS, time-of-flight MS, and reflectron time-of-flight MS. Another section is devoted to the detection of charged particles by standard devices like the Faraday cup, electron multipliers, microchannel plates, and scintillation techniques. With the presented methods it is possible to characterize the cluster beam according to its mass, velocity, and energy distribution. The chapter concludes with a discussion of

those methods which are best suited for mass-selected cluster deposition experiments.

Chapter 5 is then dedicated to the application of cluster beams for thin film deposition and surface modification. It starts with a phenomenological description of the possible processes taking place in the event an ion hits a surface. The possible advantages and disadvantages of using clusters instead of atomic projectiles are briefly introduced. The first section discusses the effect of the kinetic energy of the particles on the final morphology of the surface or of the thin film. The collision energy is also responsible for how much of the cluster's identity itself is retained in the impact process. Even if the cluster does not disintegrate in the collision it may still become deformed by flattening or by diffusion and coalescence. Most of the data presented here rely on molecular dynamics simulations. Experimental investigations using scanning probe microscopy and high-resolution electron microscopy of diffusion and coalescence are presented in the following section.

First, the results on the deposition of large antimony, gold, and silver clusters on highly oriented pyrolytic graphite (HOPG) are shown (size distributions around 2300 and 250 atoms for Sb and Au, around 300 atoms for Ag). The clusters form ramified islands on the surface, which consist of particles with a diameter of about 5 nm, independent of the cluster size distribution deposited. These results suggest the existence of a well-defined critical size of particles for coalescence, which might be due to a liquid-solid phase transition as a function of cluster size. Computer simulations find very large diffusion coefficients for these large clusters on HOPG, suggesting that the observed structural features might be due to the Brownian motion of quasi-rigid particles, which stick reversibly after a binary encounter.

Second, results on the deposition of small size-selected silver clusters on a Pt(111) surface are presented. They show that it is indeed possible to achieve a "soft-landing" of small mass-selected clusters from a molecular beam using a pillow made up of rare gas layers. However, the final morphology of the clusters after removal of the pillow is still very much influenced by the cluster-substrate interaction. Furthermore, by using clusters with defined hyperthermal energies it is possible to create surface defects, which can act as pinning centers for island formation of diffusing clusters.

In the next two sections the main topic is the formation of thin films by cluster beam deposition at either low or at high kinetic energies. To achieve such a high density of clusters to produce a thin film, mass selection is not possible at the moment, but by the adjustment of the experimental parameters it is possible to generate high-intensity beams with small mass distributions. Deposition of this beam under low-energy (thermal) conditions should lead to a nanocrystalline film, which resembles the properties of the cluster size distribution, assuming that no coalescence takes place. One example is presented for thin films assembled of silicon clusters, where the shift in the position of the Raman peaks is observed as a function of the cluster size distribution used for deposition. Further examples are shown for thin films made up of carbon clusters and metallic clusters (antimony, bismuth). Finally, the magnetic properties of films made up of Fe, Ni, and Co clusters and the optical properties of composite nanocrystalline films are discussed.

One advantage of cluster beams compared to atomic beams is the high mass-to-charge ratio that can be achieved. This leads to

sputtering yields at high kinetic energies (from several keV up to several hundred keV), which are substantially higher. Furthermore, owing to lateral sputtering effects the smoothness of surfaces prepared by cluster beam sputtering is higher than with conventional beams. A further substantial increase in sputtering yield can be achieved by using reactive cluster ions (e.g. SF_6 clusters), where the chemical reaction of the cluster material with the surface atoms leads to the formation of volatile compounds (e.g. cluster impact lithography). It has also been shown that the deposition of ionized clusters with energies of several keV leads to very smooth thin layers of cluster material. These films have a better adhesion to the substrate compared to films generated by conventional Knudsen techniques. Therefore the ionized cluster beam deposition technique has been adopted by several groups and even dedicated types of apparatus are available commercially. Despite the observed advantages, the role of the cluster size distribution for the outcome of the film formation process is still unclear.

In the final chapter (chapter 6) the advantages and disadvantages of the cluster beam technique are summarized, and possible future applications for the synthesis and the processing of nanostructured materials are discussed.

An Appendix contains a list of useful material properties relevant for the design of cluster sources.

The book gives a sound introduction to the available and necessary techniques for cluster beam processing and generation of nanostructured materials. It can be recommended for the novice, interested in this new field, and also for researchers already working in this area, because it summarizes most of the results in this field up to date and the references are not only sufficient and appropriate, but more than complete. The overall appearance with regard to presentation, grammar, and print is very good and the chapters are well ordered.

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