Nanostructured Materials from Clusters: Synthesis and Properties

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The low energy cluster beam deposition technique (LECBD) is developed to prepare original nanostructured systems from clusters pre-formed in the gas phase. The nucleation and growth mechanism specific of the cluster deposits is studied in view to control the nanostructured morphology of the cluster assembled films, especially for future applications to high areal density devices. Examples of the synthesis and properties of metallic nanostructures as well as covalent ones are presented. In the first case, systems from noble metal clusters (Ag, Au, and $\text{Ag}_x\text{Au}_{1-x}$) and transition metal based clusters (Co, SmCo_5) assemblies are studied for their original optical or magnetic properties, respectively. In the second case, covalent semiconducting films exhibiting specific electronic structures are obtained by Si, C, and $\text{Si}_x\text{C}_{1-x}$ cage like clusters (fullerenes and heterofullerenes) depositions.

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1. Introduction

The physics and chemistry of nanoscale systems has advanced significantly over the last ten years and there are attractive prospects of translating these original scientific developments into a new generation of high technology materials and processes. Since nanotechnology is a generic technology, it cuts across several industrial sectors, from chemistry to electronics, from sensors to biotechnologies and advanced nanostructured materials. In this general context, the design and fabrication of nanostructured systems and the study of their specific properties are playing an increasingly important role. Solution phase chemical synthesis has been successfully used to prepare monodisperse pure or alloyed nanoparticles of various nature (*i.e.* metallic, covalent semiconducting, oxides),^{1–5)} as well as physical methods such as vacuum atomic or molecular deposition techniques, mechanical synthesis (*i.e.* ball milling, severe plastic deformation, . . .)⁶⁾ or thin film nanoengraving techniques (*i.e.* using focussed ion or electron beams, AFM, . . .).^{7–9)} As for the chemical syntheses, they generally offer the unique advantage to prepare large quantities of nanostructured matter while the physical ones mentioned above (except the mechanical synthesis) are very often limited to the preparation of thin films. However, these last methods seems still promising in terms of specificity of the nanoparticle structures and properties related with their non equilibrium preparation conditions generally characterized by relatively high cooling rates. Among various vacuum deposition technique, a special attention is drawn in this paper to the Low Energy Cluster Beam Deposition (LECBD) which have been successfully developed in the past ten years to prepare original nanostructured materials.^{10–14)} This technique consists on the deposition on various substrates in ultra high vacuum (UHV) of supersonic nanosize clusters pre-

formed in the gas phase using combined vaporization-inert gas condensation sources. In this case, cooling rates as large as 10^{10} K/s (*i.e.* when using a laser vaporization source)¹²⁾ can be at the origin of the formation of clusters with non conventional structures and properties. Moreover, in the low energy deposition regime (*i.e.* kinetic energy per atom of the cluster lower than 1 eV), clusters are not fragmented upon impact on the substrate leading to the formation of supported nanostructures (or nanostructures embedded in matrices) which retain the memory of the structure and properties of the free incident clusters.^{13, 15–18)}

In this paper we report on the synthesis of various nanostructures using the low energy cluster beam deposition technique as well as their specific properties. Examples of covalent semiconducting nanostructured systems based on pure silicon or mixed silicon-carbon cage like clusters (fullerenes and heterofullerenes), with original electronic structures and properties, are presented.^{19–22)} Also, nanostructured systems from metallic clusters for applications to magnetic (*i.e.* Co or SmCo_5 clusters)^{23–26)} or optical nanostructures (*i.e.* Ag, Au, $\text{Au}_x\text{Ag}_{1-x}$ clusters)^{27–30)} are described. In some specific cases, both static and dynamic aspects³¹⁾ of the properties of nanoscale systems have been investigated. Moreover, experimental efforts are efficiently complemented by theoretical approaches or/and numerical simulations which benefits of the significant computer technology developments over the last decades. In particular, *ab initio* calculations which allow to accurately describe the atomic and electronic structures of nanoscale systems have been applied in the case of covalent semiconducting Si and Si-C clusters,²¹⁾ as well as TDLDA (Time Dependent Local Density Approximation) method to interpret the optical properties of noble metal clusters (Au, Ag).³²⁾ As for the nucleation and growth process of cluster deposits in the LECBD regime leading to the characteristic

nanostructured morphology of the cluster assembled films, it is simulated using both pure ballistic deposition and molecular dynamics models to describe the system at different scales down to the atomic one.¹³⁾ Finally, on the basis of the relatively good knowledge on the formation and properties of nanostructured systems from clusters, new routes for the realization of cluster based high areal density devices are tested and the preliminary results presented.

2. Experimental Procedures

Cluster assembled films are prepared by deposition of low energy clusters preformed in the gas phase (LECBD) using a specially designed equipment schematically represented in Fig. 1. For that purpose, a cluster generator based on a combined laser vaporisation-gas condensation source has been developed to produce intense supersonic jets of nanoclusters with sizes ranging from a few tens to a few thousands of atoms (diameter ≈ 1 to a few nm), typically. Briefly, a YAG laser ($\lambda = 532$ nm, pulse duration $\approx$ a few ns, frequency ≤ 30 Hz), or a Ti-Sapphire laser ($\lambda = 790$ nm, pulse duration $\approx$ a few μ s, frequency ≤ 30 Hz) are used to vaporize the target rod mounted in the source chamber (Fig. 1). Combined with the laser pulse, a high pressure gas pulse (He, 3 to 6 bars, pulse duration 200 to 500 μ s) is injected in the source chamber to rapidly cool the plasma generated at the target surface and to nucleate clusters which are subsequently completely cooled and stabilized in the supersonic expansion taking place at the exit nozzle of the source. The main feature of this type of cluster source compared to other ones currently used (thermal, sputtering) is the very high cooling rate up to about 10^{10} K/s which governs the formation of original nanoscale systems in non-equilibrium conditions. From the key parameters of the source (laser pulses, gas pulses/continuous gas flow, delay between both pulses, and geometries of the nucleation chamber in the source and the nozzle), it is possible to control the cluster size distributions measured in the high resolution time of flight (TOF) mass spectrometer mounted immediately after the skimmer (Fig. 1). For that purpose, neutral clusters are photo-ionized using a tunable excimer-dye laser, then deviated and accelerated at the entrance of the TOF-line. At this stage, photo-ionization near threshold and photo-fragmentation experiments are performed on free clusters to characterize their structures and properties.

In the particular case of mixed cluster production (bimetallic, Si-C), both methods have been developed based on the use of a compound target directly mounted in the source or a special source with two independent targets simultaneously vaporized by two independent lasers (Fig. 1). When using the technique with a compound target, it has been verified for all bimetallic systems studied (*i.e.* Pt-Pd,³³⁾ Au-Ni,³⁴⁾ Au-Ag,³⁰⁾ Co-Sm²⁶⁾) that the cluster exhibit the same composition that the target rod one. However, depending on some specific effects such as segregation, atoms can be inhomogeneously distributed in the cluster.

In the particular case of LECBD-experiments, only neutral clusters having the very low energy gained in the supersonic expansion at the exit of the source ($\leq$ a few 10^{-2} eV per atom) are deposited on various substrates in the UHV-deposition chamber mounted on line with the cluster generator-TOF ar-

Fig. 1 Schematic view of the cluster generator based on a combined laser vaporisation/inert gas condensation source, associated to a high resolution time of flight mass spectrometer (reflectron) for the studies of free clusters and a UHV-deposition chamber for cluster assembled film preparations. The source can operate with one or two independent laser/target arrangements for the production of pure clusters as well as mixed clusters. Some characterization techniques of the films are available *in situ* in UHV: RHEED diffractometry, STM-AFM near field microscopy, Auger-XPS spectrometry. A UHV-transfer system is used for sample transfers to ex situ equipments. An electron-beam evaporator *in situ* in UHV is used for co-deposition experiments to produce films of clusters embedded in various media.

range (Fig. 1). In our experiments, the complete distributions of neutral clusters (nearly Gaussian in shape and rather narrow from our laser vaporization generator) are directly deposited on the substrates to grow films, which allows to reach relatively high deposition rates (0, 1 nm/minute to 0, 1 nm/seconde) for all kinds of clusters. Moreover, by co-depositing on the same substrate an atomic beam emitted by the e-beam evaporator mounted in the deposition chamber (Fig. 1), it is possible to produce films of clusters embedded in various matrices (metallic, transparent oxides). Since both cluster and atomic beams are independent, this last technique allows to produce any kind of cluster/matrix system, even with miscible elements, in a wide range of cluster concentration.

For the study of the nucleation and growth mechanism characteristic of the LECBD-regime, the nanostructured morphologies of the cluster deposits as a function of the deposition parameters (nature, mean size, and flux of the incident free clusters, nature and temperature of the substrate) are observed *in-situ* using the STM-AFM near field microscope mounted directly on the UHV-deposition chamber (Fig. 1). Complementary high resolution transmission electron microscopy observations (HRTEM) are performed *ex-situ* to characterize the atomic structure of isolated supported clusters and cluster assembled nanostructures. In this

case, deposits below the 2D-percolation threshold (coverage rate $< 50\%$) are performed on amorphous carbon coated grids and subsequently protected by a thin amorphous carbon layer on top before removing in air. Structural characterizations on collections of clusters by X-Rays techniques (diffraction and absorption (EXAFS)^{23,35,36}) using the synchrotron radiation facilities at LURE-Orsay, France) are generally performed in addition to the structural characterizations by HRTEM of isolated individual supported clusters.

As for the studies of the electronic and vibrational structures of the cluster films, especially in the case of covalent semiconducting systems from Si and Si-C clusters, Photoelectron (XPS), Infrared (IR) and/or Raman spectroscopies are applied.^{19,20} XPS measurements are performed *in-situ* in UHV on uncoated supported clusters, while a specific sample geometry is used for IR-Raman measurements. This last one consists on a cluster film deposited on a transparent substrate and subsequently coated by a silver film which acts as a mirror for the measurements with the beam through the transparent substrate.

Magnetic nanostructures from pure cobalt clusters or mixed cobalt-samarium clusters are studied using various complementary techniques in order to investigate on the magnetic behaviour from an isolated individual cluster to an assembly of non-interacting or interacting clusters. For that purpose, a ultrahigh sensitivity magnetometry technique based on microSQUIDS devices has been developed³⁷) to detect for the first time the magnetic signal of one single nanoparticle with size as low as 1000 atoms (*i.e.* one Co-cluster of ≈ 3 nm in diameter).³⁸) Such a challenge is achieved by embedding the Co-clusters directly in the metal (niobium) constituting the superconducting microSQUID loop at low temperature (≤ 7 K) to considerably improve the cluster-microSQUID coupling. As for the magnetic measurements on cluster assemblies, conventional SQUID or VSM magnetometry techniques are used complemented by X-Rays Magnetic Circular Dichroism (XMCD) measurements³⁸) to probe the magnetism of clusters at a local scale.

3. Nucleation and Growth Mechanism of Cluster Films

Since the properties of cluster assembled material films are strongly related to their nanostructured morphologies resulting from a specific nucleation and growth process, one has to figure out what is likely to occur when clusters are deposited on a surface in order to understand and consequently to control thin film morphologies.³⁹) A first idea at the origin of the studies on the formation of clusters assembled films in the low energy deposition regime (LECBD), consisted in considering that large clusters (several hundred to several thousands of atoms) deposited on a surface do not move, leading to film growth by random paving of the substrate. Moreover, ideally, by depositing clusters with a low kinetic energy,^{17,40,41}) one can expect to preserve the size and consequently the original properties of those clusters from the free to the supported state.¹²) However, whereas this idea of a random pavement of a surface can be verified in some cases, it is too simplistic in most of them, mainly because of the diffusion of the clusters on the surface of the substrate. Theoretical and experimental studies have shown that two main physical processes

have to be taken into account: the diffusion of the clusters on the surface and the interaction between supported clusters.⁴⁴) The morphologies of the films will differ with the relative magnitude of these parameters, thus depending on the choice of the cluster-substrate system. To illustrate this statement, two extreme experimental cases are compared in this section: gold nanoclusters deposited in UHV-conditions on graphite (HOPG: Highly Oriented Pyrolytic Graphite) and Au (111) surfaces.

Figure 2 shows STM-images of the characteristic morphology of a film (Au-equivalent thickness: 0.5 nm) obtained by deposition on HOPG at room temperature of a size distribution of gold-clusters centered around Au₍₂₅₀₎ (diameter ≈ 2 nm). The film is composed by large ramified islands whose branches are made of the juxtaposition of individual particles resulting from the coalescence of several incident clusters (10 to 100). Increasing the thickness of the films leads to an increase of the island size without significant change of the island density on the surface. Previous works on Sb_N-clusters deposited on HOPG have shown that such ramified structures are well described in the framework of kinetic Monte-Carlo (KMC) simulations including deposition, diffusion and aggregation of the clusters as simultaneous processes.^{13,15,18}) From a comparison between KMC-simulations and experiments, one can extract useful information on the mechanisms occurring during thin cluster-film formation. As an example, in the particular case of gold-cluster films on HOPG, different conclusions have been drawn: (i) the diffusivity of gold clusters is found to be comparable to that of single adatom, (ii) when two particles collide they stick them irreversibly (explaining the ramified structures observed), (iii) likewise, and even more important, island consisting of as many as 100 clusters should exhibit significant mobility.^{49,50}) In such system, the flux or the diffusion coefficient have been identified as “kinetic handle”, since for example by increasing the flux or decreasing the diffusion coefficient (*i.e.* by lowering the substrate temperature), one can adjust the saturation number

Fig. 2 STM-images ($1500 \text{ nm} \times 1500 \text{ nm}$) of a 0.5 nm thick gold film prepared by Au₍₂₅₀₎-cluster deposition on HOPG-graphite at room temperature with a flux $F = 10^{-3} \text{ nm} \cdot \text{s}^{-1}$. A magnification of a ramified island is presented in insert ($100 \text{ nm} \times 100 \text{ nm}$).

Fig. 3 STM-images ($100\text{ nm} \times 100\text{ nm}$) of gold thin films produced by $\text{Au}_{(750)}$ -cluster depositions on $\text{Au}(111)$ at room temperature with a flux $F = 10^{-3}\text{ nm}\cdot\text{s}^{-1}$, for different equivalent thicknesses (e_q): (a) $e_q = 0.01\text{ nm}$; (b) $e_q = 0.03\text{ nm}$; (c) $e_q = 0.08\text{ nm}$; and (d) $e_q = 3.4\text{ nm}$.

of islands grown on the surface.

Figures 3(a)–(d) present STM-images of $\text{Au}_{(750)}$ -cluster (diameter $\approx 2.9\text{ nm}$) thin films deposited on $\text{Au}(111)$ substrate at room temperature, for various Au -equivalent thicknesses (0.01 to 3.4 nm). In this case, no fractal nanostructures are observed, the film being composed by a high density of randomly distributed isolated particles. A careful STM-analysis reveals that each supported particle corresponds to one incident free cluster. Thus, no aggregation of the incident clusters on the surface takes place, suggesting that the clusters do not diffuse on gold to form islands. Moreover, time dependent STM-observations at room temperature of the same surface area confirms this last statement and points out that two neighboring clusters do not coalesce to form a larger particle. Consequently, the films are built from a random pavement of the surface⁵¹⁾ that explains the granular structure of the thick film as observed in Fig. 3(d). Assuming a cluster as a super atom (*i.e.* neglecting the macroscopic structure of the cluster), the film morphology can be roughly predicted using a simple ballistic deposition model.⁵²⁾ However, since in such model the details of interatomic interactions (cluster-cluster and cluster-substrate interfaces) are not accounted for so far, complementary Molecular Dynamics Simulation have been performed in order to get more insight on the shape, the structure and the orientation of the supported gold-clusters. More specifically, we have shown that for a low impact energy (which corresponds to the experimental situation), the final nanostructured morphology of a thick cluster layer (above the 2D-percolation threshold) depends on the size of the incident free cluster.⁵³⁾ Since the cluster size can be experimentally adjusted in the gas phase, from the source, this study reveals the potentiality of the LECBD-technique to control the growth of nanostructured thin films.

Finally, from both characteristic cluster deposition experiments described above, it clearly appears that cluster diffu-

sion strongly depends on the nature of the substrate. In the case of HOPG, the π -bonding is not efficient enough for the cluster pinning leading to nanoparticles weakly bonded to the graphite. Consequently, the large diffusion of the clusters on the surface leads to deposits composed by ramified nanostructures. In the case of gold substrate, the interaction of clusters with the surface is stronger. This is consistent with the fact that (111) facets of the gold-cluster (assuming a cuboctahedron shape) exhibits a lattice parameter close to the (111) surface of the gold-substrate favoring the cluster/substrate epitaxy. The low diffusion coefficient is then directly related to a good lattice-parameter matching. This last statement is in complete agreement with recent classical molecular dynamics simulations using a simple Lennard-Jones potential, where the importance of the lattice-parameter mismatch between the cluster and the surface is emphasized.⁵⁴⁾ Consequently, by adjusting the nature and the size of the incident free clusters combined with the nature of the substrate, one can get sub-monolayer thin films composed by islands (ramified or not, depending on the coalescence process between adjacent clusters⁵⁵⁾ or by isolated nanoparticles. These attractive aspects of the LECBD-films seems promising for future applications to the preparation of original quantum devices.

4. Optical Nanostructures from Noble Metal Clusters

Noble metal particles exhibit specific optical properties due to the multipolar collective excitations arising from the dielectric confinement.⁵⁷⁾ In the nanometer range the photoabsorption spectra are dominated by an absorption band whose position and width are ruled by the intrinsic properties of the clusters and the surrounding medium (surface plasmon or Mie-resonance). These features appear to be size-dependent, although no size effect is predicted by the classical Mie's theory in the quasistatic limit, except for a mere volume scaling factor. These measured size effects which reflect those of the electronic structure have indeed a quantum origin. In contrast with alkali clusters for which the plasmon frequency exhibits a noticeable red-shift with decreasing cluster size due to the spill-out phenomenon,⁵⁸⁾ this trend is reversed in the case of free Ag_N^+ and Au_N^+ clusters,^{59,60)} namely a slight blue-shift is observed, reflecting the influence of the d-electrons. The understanding of the optical properties of pure metal particles makes the extension of this study to bimetallic clusters in the small size domain very interesting. Bimetallic particles can form either alloys or segregated (referred to as coated, or core-shell particles) systems (see *i.e.* Refs. 61) to 63)). Up to now, most of the experiments on alloyed and coated Ag/Au systems are realized for particles larger than 5 nm in diameter.^{62,64)} Here we report on the size evolutions of the optical properties of alumina-embedded mixed silver-gold clusters ($\text{Au}_x\text{Ag}_{(1-x)}$, with $x = 0, 0.25, 0.50, 0.75$, and 1) with mean optical diameters between 1.5 and 7 nm, prepared by LECBD.

Clusters and alumina matrix are co-deposited on a substrate at room temperature as described in Section 2. The metal volumic fraction is chosen to be less than 5% by controlling both deposition rates, in order to reduce the cluster coalescence effect and to deduce the optical properties of non-interacting isolated particles. Optical absorp-

Fig. 4 Optical absorption spectra of $(\text{Au}_x\text{Ag}_{1-x})_N$ -clusters in alumina films for various relative compositions x , and size distributions: (a): Ag_N ; (b): $(\text{Au}_{0.25}\text{Ag}_{0.75})_N$; (c): $(\text{Au}_{0.5}\text{Ag}_{0.5})_N$; (d): $(\text{Au}_{0.75}\text{Ag}_{0.25})_N$; and (e): Au_N . The mean optical diameter of clusters (defined as $D_{\text{opt}} = \langle D^3 \rangle^{1/3}$) is indicated for each sample.

tion spectra displayed in Figs. 4(a)–(e) for respectively Au_N , $(\text{Au}_{0.25}\text{Ag}_{0.75})_N$, $(\text{Au}_{0.5}\text{Ag}_{0.5})_N$, $(\text{Au}_{0.75}\text{Ag}_{0.25})_N$, and Ag_N -clusters/alumina films, for various cluster-size distributions, exhibit a more or less pronounced absorption band (between 2 and 3 eV) due to the surface plasmon resonance and an increasing absorption in the UV region due to interband transitions. Comparison of our spectra (for mixed clusters) with those of alloyed and segregated Au–Ag clusters reported in the literature^{65–67} highly suggests an alloying of the two metals inside the clusters. One can notice a large broadening and damping of the surface plasmon band as the cluster size decreases, especially for gold-rich clusters.²⁷ These effects are more pronounced with increasing x , indicating a more important coupling between intra and interband transitions. Moreover a noticeable blue-shift of the resonance with decreasing cluster size is observed for $x = 1$, $x = 0.5$, and $x = 0.75$. This blue-shift trend weakens steadily with increasing concentration of silver atoms inside the clusters and is completely quenched for $x = 0.25$ and $x = 0$.^{28,32,68} Such quantum size effects can be reproduced in the frame of a quan-

tum/classical theoretical approach where the conduction electrons are quantum-mechanically treated (TDLDA), whereas the optical properties of the matrix and the ionic core background (interband transitions from the d band towards the s-p conduction band, and polarization effects) are classically described through bulk-like dielectric functions.⁶⁹ The model includes the inner surface skin of ineffective screening by the ionic cores,^{28,70} and the local porosity at the particle-matrix interface.^{28,32,68} The frequency-dependence of the real component of $\epsilon_d(\omega)$ (where $\epsilon_d(\omega)$ is the interband contribution in the dielectric function of the metal) is found to be the key feature ruling the competition between the blue-shift trend induced by the skin regions of reduced polarisability, and the red-shift trend induced by the spill-out phenomenon, the net result of which leading to the quenching of the size effects in silver clusters and the increasing blue-shift with gold concentration.

Complementary investigations on the internal thermalisation dynamics of the conduction electrons have been carried out in silver nanoparticles. These measurements based on femtosecond laser spectroscopy^{71,72} lead to the determination of electron-electron thermalisation times.⁷³ The establishment of an electron temperature is taking place on a few hundred femtosecond time scale. An acceleration of the conduction electron thermalisation is observed with decreasing silver cluster size. This observed thermalisation fastening is ascribed to an increase of electron-electron scattering in small particles. The size dependence of the thermalisation time is consistent with the model mentioned above and described in details in Ref. 28).

5. Magnetic Nanostructures from Transition Metal Clusters and Mixed Transition Metal-Rare Earth Clusters

The preparation of original magnetic nanostructures and the study of their specific properties are playing an increasingly important role directly related with the large number of potential applications in various fields such as information storage and magnetoelectronic devices.^{5,14,74–76} On the fundamental point of view, the magnetic behaviour of individual isolated nanoscale systems was mainly theoretically approached while experimental investigations are limited by the sensitivity of the magnetic characterization techniques. Moreover, in bulk magnetic materials (3D), magnetostatic and bulk magnetocrystalline energies are the main sources of anisotropy whereas in lower dimensionality systems such as thin films (2D), wires (1D) or clusters (0D), strong surface effects are expected. Consequently, the necessity of studying one single nano-object to provide information on the different contributions to the magnetic anisotropy is of particular importance, especially for future applications because of the superparamagnetic limit characteristic of such small systems.⁷⁶ In fact, when decreasing the size of the particle down to the nanometric range, the anisotropy energy $K_u V$ (where K_u is the anisotropy constant and V the volume of the particle) which act to fix the magnetization along an easy axis is counterbalanced by the thermal energy kT responsible of magnetization fluctuations between easy axis. The blocking temperature T_B indicating the upper limit above which

the nanoparticles behave superparamagnetic is generally of the order of 10 K to a few tens of K. Consequently, in the nanosize range, a first challenge prior to applications consists to develop novel magnetic materials with a rather high anisotropy in order to remain magnetically oriented up to room temperature or above.⁷⁶⁾

Recently, the development of novel magnetometers based on microSQUID^{37,75)} with sensitivity approaching 10^{-20} A·m² (10^3 Bohr-magneton) which are capable to detect the magnetization reversal of one single nanoparticle³⁸⁾ has opened a promising window in this field of “experimental nanomagnetism”. For that purpose, thin 20 nm Co-cluster/Nb-matrix films were prepared using the co-deposition technique described in Section 2 and subsequently e-beam micro-lithographed to pattern a large number of microSQUID loops (Fig. 5(a)). The concentration of Co-clusters is low enough ($<0.1\%$) to avoid any interaction between them. Moreover, only the magnetic flux coupling of a cluster located in a micro-bridge (Fig. 5(a)) is high enough to allow the detection of its individual magnetization reversal and the measurement of the corresponding spatial switching field distribution. 3D-angular dependence of the switching field was measured by rotating the external magnetic field in and out of the microSQUID plane (Fig. 5(b)). This last diagram evidences one easy magnetization direction along the H_z axis and one hard magnetization direction along the H_y

axis. Assuming that $T = 0$ K (the experimental temperature being 35 mK), and a uniform rotation process of the particle magnetization, we use the Stoner and Wohlfarth model generalized in three dimensions⁷⁷⁾ to perform a rather good fit of this spatial distribution. We deduce a second order anisotropy energy: $E(\mathbf{m})/v = -K_1 m_z^2 + K_2 m_y^2$, where v is the magnetic volume of the particle, $\mathbf{m}$ a unit vector in the magnetization direction, and $K_1 = 2.1 \cdot 10^5$ J/m³, $K_2 = 0.5 \cdot 10^5$ J/m³ the anisotropy constants along the easy and hard axes, respectively. Finally, we can conclude that a Co-nanoparticle embedded in a niobium matrix mainly behaves as a macrospin with a bi-axial anisotropy corresponding to a second order anisotropy energy. Let us discuss the physical origin of such anisotropy. First we can rule out the usual cubic magnetocrystalline anisotropy for fcc-cobalt^{23,35)} since this fourth order term is one order of magnitude larger than the experimental one. Secondly, by considering the nearly spherical shape of the Co-clusters, the shape anisotropy term can also be neglected. Moreover, because the elastic constants of the bcc-niobium are smaller than the fcc-cobalt ones, the contribution of the magneto-elastic anisotropy energy resulting from the matrix induced isotropic stresses on the particle should be small. Consequently, the experimental anisotropy measured for our individual Co-clusters is probably related to an interface anisotropy resulting from the symmetry breaking at the cluster surface.

Thick samples consisting of Co-cluster assemblies diluted in a niobium matrix (Co-volumic concentration $\approx 5\%$) were prepared in view to perform structural and complementary magnetic characterizations. Structural studies^{23,35)} using High Resolution Transmission Electron Microscopy (HRTEM), X-rays diffraction and absorption (performed using the french national synchrotron laboratory facilities: LURE, Orsay), indicate that the deposited Co-clusters in the bcc Nb-matrix can be described as fcc-truncated octahedrons containing about one thousand atoms (diameter ≈ 3 nm) distributed as follows: 36% are in the pure Co-core of the grain, 27% participate to a Co₄Nb-phase in the sub-surface layer, and 37% participate to a Co₆Nb₇-phase in the surface layer. Moreover, from Vibrating Sample Magnetometry (VSM) measurements on the same Co-clusters/Nb-matrix films, we can conclude that the Co-Nb alloyed interface is a “magnetically dead” layer which is probably at the origin of the reduced “magnetic size” distribution observed with respect to the TEM-one.³⁵⁾ Additional X-Rays Magnetic Circular Dichroism (XMCD) experiments were performed at the European Synchrotron Radiation Facilities (ESRF, Grenoble-France). XMCD is used in our case as a local magnetometry technique operating in the low temperature range (*i.e.* $T < 8$ K), where the superconducting fluctuations due to the Nb-matrix prevent any conventional magnetization measurements. Finally, from the hysteresis loops measured in the temperature range 5–50 K, we deduce the remanent magnetization (Fig. 6) and an effective anisotropy constant $K_{\text{eff}} = 2.10^5$ J/m³ for the Co-clusters. Note that K_{eff} is of the same order of magnitude than K_1 previously found from the microSQUID measurements on an individual Co-nanoparticle.

The Co-clusters/Pt-matrix system which is also a miscible couple has been studied in the same conditions⁷⁸⁾ to verify

Fig. 5 (a) Schematic view of a microSQUID loop patterned out of a 20 nm thick Co-clusters/Nb-matrix film by electron beam lithography. The highest detection sensitivity is obtained for nanoclusters located in the micro-bridges as shown in the figure. (b) 3D-distribution of the switching field for an individual Co-cluster (diameter ≈ 3 nm, ≈ 1000 Co-atoms) embedded in the micro-bridge.

Fig. 6 Remanent magnetic moment plotted versus temperature. The signal is first normalized taking: $m_r(8 \text{ K})_{\text{VSM}} = m_r(8 \text{ K})_{\text{XMCD}}$. One can see that the continuous line curve fits both VSM (full dots) and XMCD (open dots) measurements. From this fit, one can deduce the anisotropy constant $K_{\text{eff}} = 2.0 \pm 0.3 \cdot 10^5 \text{ J/m}^3$ (see details of this procedure in Ref. 38)).

the validity of the core-shell model suggested above to account for the magnetic properties in such nanogranular films. Finally, from both Co/Nb and Co/Pt samples we found that cluster magnetization can be written in the form: $M_s(T) = x M_s^{\text{core}}(T) + (1 - x) M_s^{\text{shell}}(T)$.³⁵⁾ For Co/Pt, one atomic layer is expected to diffuse at the interface giving $x = 0.63$. In addition, we assume that $M_s^{\text{core}}(T) = M_s^{\text{bulk}}(T)$ leading to a magnetization enhancement at the interface $M_s^{\text{shell}}(0) = 1900 \text{ kAm}^{-1}$ (to compare with $M_s^{\text{core}}(0) = 1430 \text{ kAm}^{-1}$). On the contrary, in the Co/Nb case, $M_s^{\text{shell}}(0)$ is found equal to zero and $x = 0.36$, because of the presence of two “magnetically dead” alloyed monolayers at the cluster-matrix interface, leading to the very low experimental value observed $M_s(0) = 515 \text{ kAm}^{-1}$.

Since the superparamagnetic limit prevents the use of pure transition metal particles with sizes lower than 10 nm to prepare high density storage media,⁷⁶⁾ intermetallic compounds with strong magnetocrystalline anisotropy such as rare earth-transition metal alloys have been tested. For that purpose, SmCo_5 -nanoclusters prepared from a bulk SmCo_5 -target mounted in the laser vaporization source have been embedded in niobium co-deposited films.²⁶⁾ Due to the segregation of samarium atoms at the cluster surface, a loss of magnetization is observed in the as deposited nanostructured samples compared to the bulk phase. However, post annealing treatments in UHV up to 570°C lead to an improvement of the crystallinity of the Sm-Co nanoparticles, and consequently to a significant increase of their magnetic anisotropy at the origin of a blocking temperature T_B larger than 300 K .⁷⁹⁾ This is illustrated in the Fig. 7 showing the characteristic evolution of the magnetization loops with an increase of the coercive field as a function of the annealing temperature for a SmCo_5 -clusters/Nb-matrix film.

6. Semiconducting Nanostructures from Silicon/Carbon Cage Like Clusters

Si-C materials in crystalline and amorphous forms have been extensively studied over twenty years.⁸⁰⁾ Such structures

Fig. 7 Hysteresis loops obtained by conventional SQUID-magnetometry measurements at 20 K and 300 K for films of SmCo_5 -clusters embedded in Nb-matrix. The volumic concentrations of SmCo_5 -clusters were low enough ($\leq 5\%$) to avoid cluster coalescence effects. (a) as deposited film; (b) film subsequently annealed *in situ* in UHV at 570°C for 30 minutes.

are good candidates for large band gap electronic devices as well as very hard materials. In all SiC-polytypes, the lattice is formed by a periodic arrangement of silicon and carbon atoms in a sp^3 tetrahedrally bonded network with a perfect chemical ordering. $\text{Si}_x\text{C}_{1-x}$ compounds with $x \neq 0.5$ are more complex and still debated since compositional disorder introduces homonuclear (*i.e.* C-C or Si-Si bonds) and heteronuclear bonds (*i.e.* Si-C bonds). The tendency to chemical ordering into a sp^3 -network prevails in Si-rich films. Conversely, the disorder increases in C-rich films. However, most of the samples prepared are more or less described in terms of local tetrahedral environment with additional sp^2 fused rings for rich carbon samples. In this context, original silicon carbide films were prepared by the LECBD-technique.²²⁾ These films exhibited a nanostructured morphology characteristic of the LECBD-technique with a large porosity. The minimization of the dangling bonds due to the presence of a large number of atoms at the surface of the nanograins involves a rearrangement of the classical “diamond” tetrahedral structure. This is achieved if silicon and carbon form a compact structure close to the so-called “fullerenes” structure. In the case of carbon, the fullerenes have an empty core leading to a three-fold configuration,⁸¹⁾ while silicon cages are “stuffed” with additional silicon atoms inside the cage.¹⁹⁾ This last configuration allows a four-fold structure which is more stable for silicon. For SiC-heterofullerenes, a competition between three-

fold and four-fold configurations is expected. In this case, it has been established that empty core fullerenes are stable up to twelve silicon atoms (*i.e.* $\text{Si}_x\text{C}_{60-x}$ with $x < 12$ is isostructural to C_{60}).

Figure 8 displays the mass distributions measured in the TOF mass spectrometer of the free ionized clusters $\text{Si}_x\text{C}_{1-x}^+$,

Fig. 8 Abundance mass spectra in selected windows of ionized $\text{Si}_x\text{C}_{1-x}$ -clusters for different x -values, measured using the high resolution TOF mass spectrometer associated with the laser vaporization cluster source. (a) pure carbon clusters ($x = 0$, fullerenes); (b) heterofullerenes ($x = 0.12$); (c) mixed SiC-clusters ($x = 0.5$); and (d) pure silicon clusters ($x = 1$).

for various values of x . For $x = 0$, pure carbon clusters formed by even numbers of atoms are present (Fig. 8(a)). This is one of the signatures of the fullerene family (*i.e.* cages with an empty core). Increasing x up to 0.12 reveals additional peaks corresponding to the heterofullerene family as observed in Fig. 8(b) for $\text{C}_{2n-q}\text{Si}_q^+$ -clusters with $q = 1$ and $q = 2$.⁸² The mass spectrum for $x = 0.5$ (Fig. 8(c)) corresponds to the stoichiometric compound with all the combinations between carbon and silicon (clusters with odd or even numbers of atoms).

The cluster assembled films resulting from the depositions of various distributions mentioned above have been analyzed by several complementary techniques: plasmon losses, Scattering Enhanced Raman Spectroscopy (SERS), X-ray photoelectron Spectroscopy (XPS), and Auger-electron spectroscopy (AES). Plasmon losses measurements are summarized in Table 1. These values are strongly dependent on the electron density in the films. For pure silicon cluster films, the plasmon frequency measured (17.2 eV) is close to the value for bulk silicon (17 eV). This is in agreement with the idea of stuffed fullerenes based-materials having a density close to the diamond structure one. However, this is not the case for pure carbon cluster films having a structure with an empty core. Moreover, the plasmon frequency for the sample $\text{Si}_x\text{C}_{1-x}$ with $x = 0.12$ (21 eV) is close to the pure carbon cluster film one (22 eV), since heterofullerenes exhibit a structure comparable to the pure fullerenes structure. For $x = 0.5$, we expect a combination between pure silicon clusters, pure carbon clusters and SiC clusters with a tetrahedral structure as mentioned below, leading to an intermediate value of the plasmon frequency (19.5 eV).

Figure 9 displays the Raman spectra measured on the $\text{Si}_x\text{C}_{1-x}$ -cluster films. For $x = 0.5$ three types of bonding in the supported clusters were revealed: C–C, Si–Si and Si–C. This latter corresponds to the chemical ordering part. One has to mention that no noticeable signal is observed during the measurements at low laser fluence ($P < 1$ mW with a spot diameter of about 2–4 μm .) for the sample with $x = 0.12$, near the 500–1000 cm^{-1} region corresponding to the phonon density of states (p-DOS) in SiC-compounds. In this case, Raman signal appears clearly by increasing the laser power up to 10 mW (Fig. 9). This signal is related to the phototransformation of the sample under laser irradiation (darkening of the irradiated zone). The peaks at high energy are attributed to the “graphitization effect” leading to the formation of amorphous carbon phase with the two characteristic bands labelled G (near 1580 cm^{-1}), and D (disorder) near 1300 cm^{-1} .¹¹ We also observe bands at 766–815 and 965 cm^{-1} that characterize Si–C vibrational modes. For comparison, the Raman allowed peaks in SiC 2H-4 crystal are given in Fig. 9.

The specific electronic structures of the mixed silicon-carbon cluster assembled films are probed by XPS and Auger spectroscopies. Figure 10(a) shows the Si_{2p} -core level line observed in the $\text{Si}_x\text{C}_{1-x}$ -film with $x = 0.12$. For comparison, the lines for bulk silicon (labelled Si-2) and SiC 2H-4 are reported on Fig. 10(a). The line in $\text{Si}_{0.12}\text{C}_{0.88}$ is located between the Si-2 and the SiC crystalline phase ones. Figure 10(b) displays the C_{1s} -core level line observed in the $\text{Si}_{0.12}\text{C}_{0.88}$ -film. In this case, the line just coincides with the line of HOPG-graphite (three-fold hybridisation). Figure 10(c) shows the Si

Table 1 Plasmon losses measured in various Si, C, and mixed $\text{Si}_x\text{C}_{1-x}$ -cluster films. The values for bulk C and Si-phases are given for comparison.

	C graphite	C diamond	Si diamond	SiC 2H4	$\text{Si}_x\text{C}_{1-x}$ $x = 0$	$\text{Si}_x\text{C}_{1-x}$ $x = 0.12$	$\text{Si}_x\text{C}_{1-x}$ $x = 0.5$	$\text{Si}_x\text{C}_{1-x}$ $x = 1$
Plasmon losses (eV)	27	34	17	22.4	22	21	19.5	17.2

Fig. 9 Raman spectra of various $\text{Si}_x\text{C}_{1-x}$ -cluster films for different x values (the same than those in Fig. 8). For comparison, SiC Raman lines in the bulk crystalline phase (SiC 2H-4) are also displayed.

LVV-lines observed in Si-2, SiC 2H-4 and $\text{Si}_{0.12}\text{C}_{0.88}$ samples, respectively. It is well known that the Auger shift is enhanced compared to XPS due to the strong extra-atomic relaxation effects in the Auger process. The main band observed in the cluster film at 86.4 eV is slightly shifted with respect to the SiC reference (87.1 eV), and significantly differs from the one in Si-2 (91.3 eV). This result corroborates the expected Si-C bonding in our film. In Fig. 10(d) are reported the carbon KLL-lines measured in SiC 2H-4, HOPG and $\text{Si}_{0.12}\text{C}_{0.88}$, respectively. The KLL-line in the cluster film presents striking similarities with the HOPG-line even for the satellite peaks at low energy. The shoulder labelled *s* in Fig. 10(d) is partially attributed to the π -component in the electron density of states. In addition, Si LVV-fine structure is similar to a sp^3 -like configuration as expected in heterofullerenes.²¹⁾

Although the Auger and XPS spectroscopy analyses of the cluster films reveal some striking similarities with SiC 2H-4, we point out some discrepancies that could be the signature of a new SiC-phase. The amplitude of the Si_{2p} -core level shift (Si-2 being the reference) is larger in SiC 2H-4 than in $\text{Si}_{0.12}\text{C}_{0.88}$. Conversely, the amplitude of the shift is larger in the cluster film for the LVV-line. To explain such effects one has to consider that the core level shift has two origins: the chemical bonding and the extra atomic relaxation due to the electron-core hole interaction during the ejection of the photo electron. This latter (final state) is described in terms of dielectric medium.⁸³⁾ Auger lines are more sensitive to the extra atomic relaxation. A complete analysis reveals that the chemical shift between Si and C is less efficient in $\text{Si}_{0.12}\text{C}_{0.88}$ than in SiC 2H-4. For example, the presence of dangling bonds in heterofullerenes could be a plausible explanation of

Fig. 10 Si_{2p} -core level lines (a), and Si LVV-lines (c) measured by XPS and Auger spectroscopies, respectively, in Si-2, SiC 2H-4 and $\text{Si}_{0.12}\text{C}_{0.88}$ samples. C_{1s} -core level lines (b), and C KLL-lines (d) measured in HOPG-graphite, SiC 2H-4 and $\text{Si}_{0.12}\text{C}_{0.88}$ samples.

the low chemical core level shift in $\text{Si}_{0.12}\text{C}_{0.88}$ -films. Unfortunately, we have no available information about Si-C bonding in the cluster films from Raman spectra owing to the low stability of the films under laser irradiation. For the cluster films with $x = 0.5$, XPS, Auger, and Raman spectroscopies reveal a combination between Si-clusters, C-clusters and SiC-clusters having a tetrahedral structure. In this case, no heterofullerenes have been pointed out.

7. Conclusion

Nanostructured materials from clusters preformed in the gas phase exhibit original structures and properties interesting for the developments of both fundamental studies in the field of nanophysics and various applications in nano-optics-magnetism-electronics-... The low Energy Cluster Beam Deposition technique (LECBD) specially developed for the preparation of such materials offers some unique potential-

ities to stabilize new nanostructured phases with properties directly related to those of the incident free clusters. Metallic as well as covalent systems are investigated using this technique. Moreover, pure or mixed clusters are synthesized in all cases to prospect in a wide range of nanostructured materials science. The main aspects attached to the preparation and characterization of cluster assembled materials have been described in this paper, complemented by some specific examples of cluster based systems with original optical, magnetic or electronic properties. In the field of optical nanostructures, pure or mixed noble metal clusters (Au , Ag and $\text{Au}_x\text{Ag}_{1-x}$) embedded in transparent media have been studied for a better understanding of their optical responses related to plasmon excitations. The studies of magnetic nanostructures from pure transition metal clusters (Co) or mixed transition-rare earth clusters (Co-Sm) have demonstrated the capabilities for increasing the magnetic anisotropy and consequently the blocking temperature of nanosystems in view of future applications to high density memory devices and spin electronics. In this case enhanced surface effects combined with magnetocrystalline anisotropy effects are at the origin of a blocking temperature as large as room temperature for nanoparticles with diameters as low as a few nanometers. In the field of semiconducting nanostructures, cage like silicon and mixed silicon-carbon clusters (fullerenes, stuffed fullerenes, heterofullerenes) are successfully used to produce nanostructured thin films with electronic structures and properties quite different to those of the corresponding bulk crystalline phases. In prospect, electronic band gap and/or photoluminescence efficiency controls will be the positive results of such studies on covalent semiconducting cluster assembled materials. Finally, further studies to control the nucleation and growth process of the low energy cluster deposits on functionalized substrates to form 2D-organized cluster arrays could be the ultimate step to realize original quantum devices.

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