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Properties of silicon–carbon-cluster-assembled films

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Abstract. We have investigated SiC films, obtained by the low-energy cluster beam deposition (LECBD) technique, and using AFM Raman and XPS spectroscopies. We produce these films at room temperature and in an ultrahigh vacuum environment to protect them from the pollution. The inner morphology of the clusters is close to an amorphous-like structure. However, most of the theoretical models predict an sp^3 hybridization, in disagreement with our experimental results. We find that the films are composed mainly by free components formed by rich silicon, rich carbon, and rich SiC regions, respectively. In our case, the mean hybridization of the rich carbon region is mainly sp^n-like with $2 < n < 3$.

PACS. 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 81.15.-z Methods of deposition of films and coatings; film growth and epitaxy

1 Introduction

During the two past decades, a lot of experimental and theoretical studies have been carried out for the understanding and the development of a new semiconductor: the silicon carbide [1]. Amorphous silicon carbide (a-$\mathrm{Si}_{1-x}\mathrm{C}_x$) is an especially good potential candidate for applications in optical devices. In fact, its wide-band gap [2] can be adjusted by variation of the x parameter. Nevertheless, numerous hybridizations between sp and sp^3 taken by carbon atoms involve a difficult interpretation of the bonding in such material [3]. The present work is devoted to the study of films obtained by the low-energy cluster beam deposition (LECBD) [4] technique, using a laser vaporization source. Contrary to other techniques, such as chemical vapor deposition (CVD) [5], reactive sputtering [6] or ion bombardment-induced amorphization of single crystal target [7], the choice of the nature and the temperature of the substrate is completely free in the LECBD technique. Furthermore, clusters can be analyzed (in terms of size and structure) before their deposition. In order to obtain information about the morphology and electronic and vibrational structures, we have performed atomic force microscopy (AFM), X-ray photoemission (XPS) and Raman spectroscopies, respectively. The microscopy pattern reveals that the size of the supported particles is around 8 nm. The inner particle appears amorphous-like. Both Raman and XPS spectroscopies clearly evidence a local phase separation into the film, the mean stoichiometry of the film being the same as the vaporized rod (in our case, $\mathrm{Si}_{1-x}\mathrm{C}_x$ with $x = 0.5$). These results are compared to theoretical calculations for a-SiC networks.

2 Production and characterization of SiC-cluster films

The free clusters are produced in a laser vaporization source, the details of which have been given elsewhere [4]. Briefly, the hot plasma obtained by laser ablation of a polycrystalline SiC target (purity 99%), is cooled down by a high-pressure (4 to 6 bars) helium pulse (purity 99.9999%) injected into the nucleation chamber of the source. A supersonic expansion achieves the nucleation and growth processes. Some nascent ions arising from the source are analyzed in a reflectron time-of-flight mass spectrometer giving the abundance mass spectrum distribution. The mean cluster size is estimated to be around $N = 12$ ($(\mathrm{SiC})_N$), leading to diameters less than 1 nm. However, contrary to pure C and Si clusters, the nascent ion spectra are different from those obtained by photoionization of the neutral species. Thus, the true neutral cluster sizes are not known. Charged clusters being deflected, only neutrals reach the substrate without significant energy: Clusters do not fragment upon impact onto the substrate. Thus, the films grow by ballistic deposition; this leads to a random distribution of the clusters onto the substrate. This technique, called low-energy cluster beam deposition (LECBD), gives films having the memory of the free phase.

Such a memory effect has been observed in the case of pure carbon [8] and pure silicon [9] clusters. Moreover, the SiC clusters are deposited in a UHV environment so that any contamination can be avoided.

The study of the free clusters reveals a wide variety of stoichiometry x inside $(\mathrm{Si}_{1-x}\mathrm{C}_x)_N$ clusters. For stoichiometric compounds ($x \cong 0.5$), the photoinduced dissociation mass spectrometry shows a trend to a phase separation within the clusters. For example, it has been found that $\mathrm{Si}_{25}\mathrm{C}_{21}^{+}$ evaporate preferentially silicon atoms [10]. Such a result is not in agreement with the perfect chemical ordering observed in SiC bulk phase. In addition, rich carbon compounds present fullerene-like structures [11] that are never observed in the SiC bulk phase. The specific features, which are related to a cluster effect, could be expected within our films produced by LECBD.

The AFM experiments were carried out on a Nanoscope III Multimode of Digital Instruments, and the SiC clusters were deposited onto highly oriented pyrolitic graphite (HOPG) substrates. Moreover, the tapping mode AFM (TMAFM) was used instead of AFM to avoid any displacement of the presumably weakly bound particles by the tip.

For XPS measurements, the clusters were deposited onto silver-coated silicon wafers, allowing us to take the Ag $3d_{5/2}$ core level as a reference. A UHV dual XPS/Auger CAMECA Nanoscan 100-type microprobe was used to analyze our samples. The film was excited by the Al K_α X-ray (1486.6 eV), and the analyzed area was about a few mm^2. To avoid any contamination, these measurements were carried out *in situ* in an ultrahigh vacuum.

A DILOR XY confocal Raman microspectrometer was used to perform Raman spectroscopy measurements. Clusters were deposited onto an LiF substrate and covered by a silver film around 800 Å thickness. The measurements were carried out through the LiF substrate, which is Raman inactive in our energy range. Since the films are highly porous and own a large surface roughness, the coupling factor between silver and SiC was great enough to observe a strong enhancement of the Raman signal with SERS (surface enhancement Raman spectroscopy). Moreover, in both XPS and Raman spectroscopies, a SiC single crystal (labeled 2H-4), taken as reference, was analyzed.

3 Experimental results

Figure 1, obtained by TMAFM, exhibits an agglomerate of clusters. Owing to the finite size of the tip, we are not able to estimate the mean cluster size directly from the pattern. However, the height profile reveals that the true cluster size is around 8 nm (typically 30 000 atoms). Complementary analysis (nanodiffraction in transmission electron microscopy) shows that isolated particles do not reveal an inner crystalline structure.

Figure 2 shows a typical Raman spectrum of the SiC-cluster film. So that the bands observed in this spectrum can be interpreted, Raman spectra of SiC crystal, on the one hand, and pure Si- and C-cluster films obtained under the same conditions, on the other hand, are shown. Thus, we can see three regions corresponding to Si-rich, C-rich and SiC-rich components, indicating a phase separation. In fact, at low wave numbers (around 500 cm^{-1}), the Raman spectrum is close to that observed in pure Si-cluster films. In the intermediate region (600–1050 cm^{-1}), the position of the broad bands observed corresponds to the narrow one observed in the crystalline SiC, indicating the presence of the $\mathrm{Si{-}C_4}$ or $\mathrm{C{-}Si_4}$ tetrahedra, i.e., a chemical ordering. The broadening of these bands is due to the amorphous-like state. At higher wave numbers, four bands located at 1100 cm^{-1}, 1350–1400 cm^{-1}, 1520 cm^{-1}, and 1600 cm^{-1} are observed. The first one is the signature of the sp^3 configuration and is also present in the pure small carbon fullerenes. Both bands, located around 1350–1400 cm^{-1} and 1520 cm^{-1}, are assigned to higher fullerenes or maybe heterofullerenes (mentioned above). The last band (around 1600 cm^{-1}) is attributed to small graphitic sheets, i.e., carbon atoms having a pure sp^2 hy-

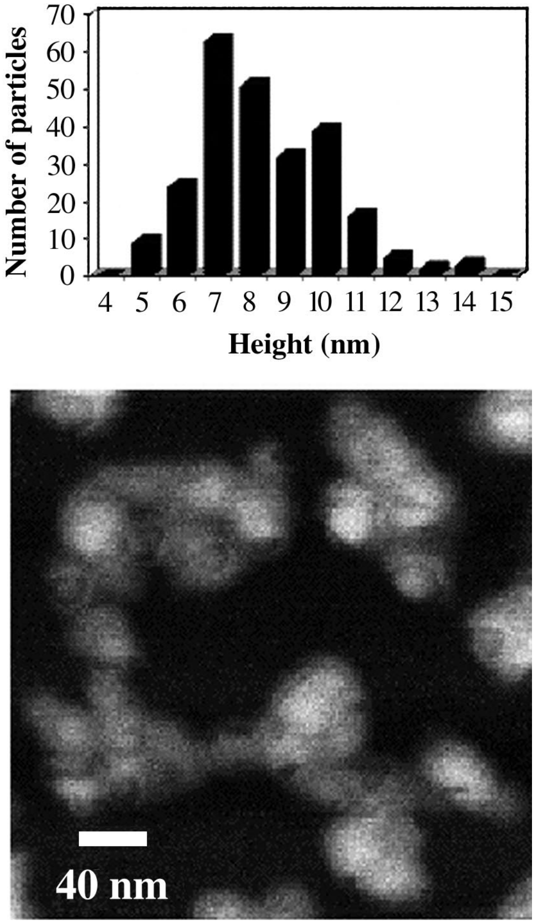

Fig. 1. AFM microscopy showing the SiC-cluster on HOPG graphite. The noticeable size is about 20 nm. This large value arises from the geometrical convolution between the tip and the cluster shape. Height variations within the agglomerates, corresponding to the individual cluster forming these agglomerates, can be measured; this allows one to obtain the height distribution. This distribution is centered around 8 nm in diameter. Assuming a nearly spherical shape, this value corresponds to the true cluster size.

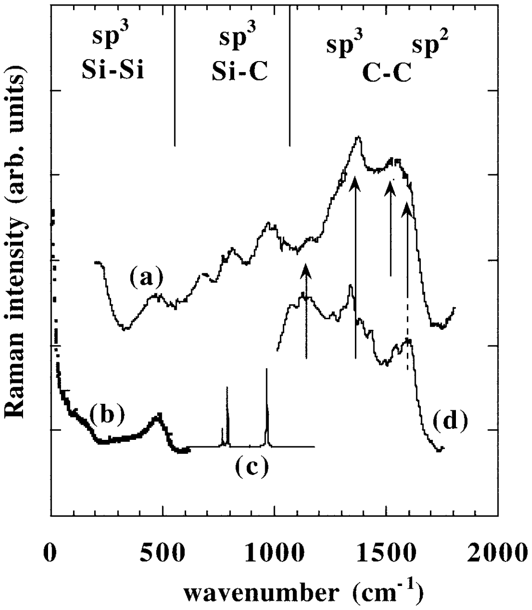

Fig. 2. (a) Raman spectrum of the SiC-cluster film. This spectrum is compared with those obtained on an Si-cluster film (b), SiC crystal (c), and C-cluster film (d). The arrows indicate the four bands pointed out in the text.

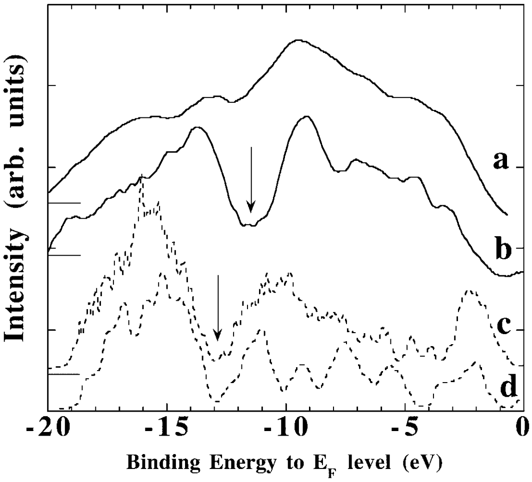

Fig. 3. Valence band spectra of SiC-cluster film (a) and SiC crystal (b). Calculated valence band spectra corresponding to 29 (c) and 357 (d) atoms are added to allow one to check that the lack of the ionic band gap in (b) is not a cluster size effect. The arrow indicates the presence of the ionic band gap. The curve (c) was obtained after broadening with a Gaussian distribution.

bridization. Thus, the presence of these three components well reveals the mixing of locally separated phases and a chemically ordered phase.

The XPS spectra near the Fermi level shown in Fig. 3 give an image of the valence band structure for both the crystalline SiC sample and the SiC-cluster film. We can observe four bands which are attributed (using a tight binding scheme) to Si_{3p}–C_{2p} (-4 eV), C_{2p}–Si_{3s} (-9 eV) and C_{2s}–Si_{3s} (-13 and -17 eV). Moreover, the disappearance of the ionic subband gap, which is present in valence band of crystalline SiC around -12 eV, is observed in the SiC-cluster film. This effect is also observed in an a-SiC structure prepared by other techniques with respect to the crystalline form.

4 Discussion and conclusion

The main results obtained by microscopy observation, X-ray photoemission, and vibrational spectroscopies deduced from our cluster-assembled films reveal two effects.

- The mean supported cluster size is about 8 nm. Let us remember that in the gas phase, the mean size of the free clusters is less than 1–2 nm. Such a difference might be attributed to several effects. The mean cluster size of the nascent ions is probably quite different from the true neutral cluster sizes, and coalescence between clusters can occur on the substrate. The amorphous-like structure tends to indicate that this coalescence occurs without merging taking place.
- Pure silicon and carbon phases and a chemically ordered component are discerned in our films through the Raman signal. The ratio of each component, which is estimated from the core level yielding ratios (Si_{2p}, C_{1s}) observed by X-ray photo emission, is 1:1:1 for Si, C, and SiC, respectively.

Now we have to understand why a local phase separation takes place here, while in ionic compounds, the chemical ordering is more favorable. Let us examine the natural dispersion Δx around the mean stoichiometry ($x = 0.5$) in free clusters $(Si_{0.5\pm\Delta x}C_{0.5\mp\Delta x})_N$ before deposition. Since the nucleation and growth processes are well governed by statistic combinations between silicon and carbon atoms, the inner composition of each cluster is well deduced from a multinomial law. Nevertheless, this dispersion is strongly reduced as far as the mean cluster size is great enough (typically > 20 atoms). Thus we assume that the strong phase separation is not yet explained by this effect. Another explanation is the so-called clustering effect [12, 13]. In order to minimize their own energy, clusters in the gas phase reorganize themselves and reduce their dangling bond; this involves a rehybridization. In the case of very small silicon clusters [9], this hybridization is still roughly sp^3 with a lot of pentagonal rings at the surface. For carbon clusters, the C_{60} ($sp^{2.3}$ hybridization) is a good candidate, since there is no dangling bond.

Thus, in our clusters, if a local phase separation occurs in the free phase, the different hybridizations and dangling bond types act as a barrier to the fusion of two clusters. Moreover, the constraint energy gained in the cluster is minimized [12, 13].

This atomic reorganization was also predicted by Finocchi *et al.* [3]. These authors have carried out a computational study on the relaxation of a piece of SiC crystal having 64 atoms, heating the cluster at 4000 K and quenching it. Finally, they have found a local phase separation.

The valence band structures (Fig. 3) in both SiC-cluster-assembled film and SiC crystals are different. Figure 3 also shows two valence band spectra obtained by tight binding calculations realized on SiC crystals having different sizes and the bulk structure. We can see from these theoretical spectra that the ionic subband gap is always present. Thus, the disappearing of this ionic gap is not a so-called size effect. This fact can be explained as follows: In the SiC cluster, owing to a phase separation, pure Si, pure C, and pure SiC contributions are superimposed. Pure elements, Si and C, give some bands filling the valley corresponding to the ionic subband gap. These results are corroborated by the calculations of Finocchi *et al.* [3] and also confirm a phase separation in our film.

In conclusion, SiC-cluster-assembled films have been obtained at room temperature using a laser vaporization source. They are formed by random cluster stacking, and the size of the supported clusters is about 8 nm. Moreover, the Raman and X-ray photoemission near the Fermi level spectroscopies are consistent with each other: They indicate a phase separation in the film.

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