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Morphological studies of nanostructures from directed cluster beam deposition

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Abstract. Tin clusters with a most probable size of 2.2 nm are formed from a magnetron plasma aggregation cluster source and deposited on the amorphous carbon and silicon surface. The morphologies of the cluster-based nanostructures formed by directed cluster beam deposition with different cluster energies and incident angles are analyzed based on the transmission electron microscope (TEM) and atomic force microscope (AFM) observation.

PACS. 36.40.Sx Diffusion and dynamics of clusters – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 81.07.-b Nanoscale materials and structures: fabrication and characterization

1 Introduction

Nanostructures produced by depositing pre-formed clusters in the size range 1−10 nm onto substrates have generated a great deal of interests [1]. The deposition process for clusters landing on the surface is different with that for atoms, giving rise to new phenomena not accessible within conventional deposition methods. With a very large degree of control on the deposition parameters, such as cluster beam kinetic energy, mass distribution and intensity, as well as the pre-formed substrate configurations, one can obtain a wide variety of cluster-assembled structures and morphologies. Studying the interaction and coalescence of clusters deposited on a substrate, one should be able to produce cluster-based nanostructures with well-controlled properties.

The dynamics of deposition and diffusion of metal clusters on the substrate surface has been the subject of increasing attention [2,3]. For low-energy (∼0.1 eV/atom) cluster deposition, the clusters suffer little distortion and induce no damage to the surface, enabling the "soft landing" of the clusters. It has been found both from experiments and molecular dynamics simulations [4–6] that for some cluster-substrate system, especially metals, such as silver, gold and antimony, on graphite, clusters exhibit high mobility on the surface. At medium energy (1−10 eV/atom), the morphology of the clusters is modified and some defects may be induced on the substrate surface. The diffusion of the clusters may be constrained by the surface damage. Therefore, depending on the impact energy and surface mobility of the clusters, either random arrays or ramified aggregates can be obtained from cluster deposition. Furthermore, patterned cluster arrays may be generated with the template of pre-formed surface defect patterns, e.g. quasi-one-dimensional "cluster wires" have been generated by trapping the clusters at the step edges of graphite surface [3].

In this paper, we investigate the morphologies of cluster-based nanostructures from directed cluster beam deposition as a function of the beam flux, the impact energy of the clusters, as well as the mobility of clusters on the substrate surface.

2 Experimental

Tin clusters are formed from a magnetron plasma aggregation cluster source [7]. The magnetron discharge is operated at a pressure of about 100 Pa in argon stream in a liquid nitrogen cooled aggregation tube. Atoms are sputtered from the target of the magnetron discharge head and clusters are formed through the aggregation process in the argon gas. The clusters are swept by the gas stream out of the aggregation tube into vacuum through a diaphragm, where the cluster growth is effectively stopped. The clusters continue to pass through a skimmer (the second diaphragm) and a beam of clusters is formed. With the appropriate configuration of skimmer and collimator,

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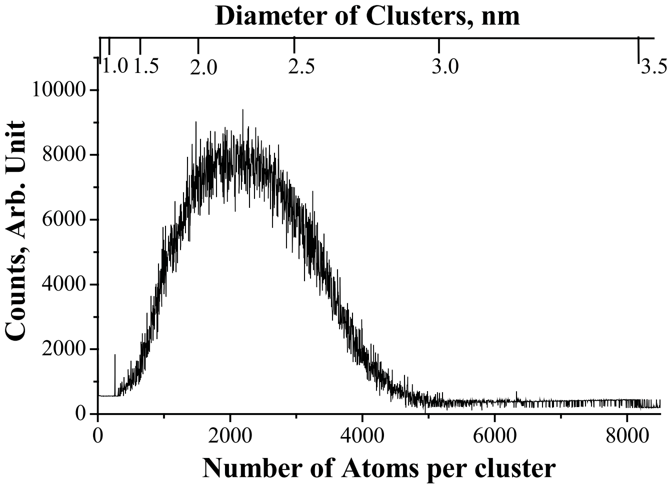

Fig. 1. TOF mass spectrum and size distribution of tin cluster ions from the magnetron plasma aggregation cluster source.

highly directed cluster beam with divergence of about 3° can be obtained. The clusters are deposited either on the amorphous carbon film supported with copper grid or on the silicon single crystal surface, both on normal and glance incidence. The kinetic energies of the clusters are controlled from low (several eV) to medium (10 keV) through a deflector/accelerator system.

The size of the clusters in the beam is measured with a time-of-flight (TOF) mass spectrometer. The beam intensity is also monitored by a quartz crystal microbalance. A deposition rate of about 10 $\text{Å}\,\text{s}^{-1}$ is obtained with a discharge power of 40 W. The morphologies of the cluster-based films are characterized by means of transmission electron microscope (TEM, JEM-200CX) and atomic force microscope (AFM, Digital Instrument Nanoscope II).

3 Results and discussion

A typical TOF mass spectrum of a beam of Sn clusters is shown in Figure 1. The clusters have a wide size distribution up to 5000 atoms (∼3 nm) with a FWHM of 2300 atoms (∼2.3 nm). Typical TEM micrographs are shown in Figure 2 for cluster assemblies deposited from low energy neutral cluster beam and 10 kV ionized cluster beam respectively, both with normal incidence. The size distributions of the deposited clusters are given in Figure 3. In all the cases, the diameters of the deposited clusters observed from TEM are much larger than those of the clusters in free beam, indicating that the clusters are effectively coalesced after they land on the surface.

From TEM micrographs, the cluster-based nanostructures have different features on the cluster size distribution and morphology for the low energy neutral beam and energetic ionized beam deposition. It suggests that their coalescence processes are different. For the low energy deposition, the clusters have smooth surfaces and spherical morphologies. It seems that the clusters undergo further quasi-free growth process which is well developed after

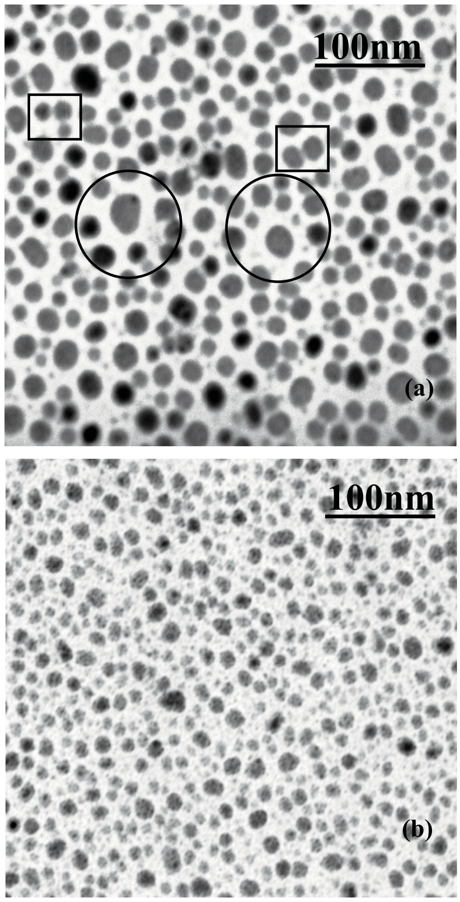

Fig. 2. TEM images of cluster assemblies from cluster beam deposition. (a) The cluster-based nanostructure is formed from low energy neutral cluster beam deposition with normal incidence. The regions marked with circles give the evidence of Oswald ripening process while those marked with rectangles give the evidence of annealing process. (b) The cluster-based nanostructure is formed from 10 kV ionized cluster beam deposition with normal incidence.

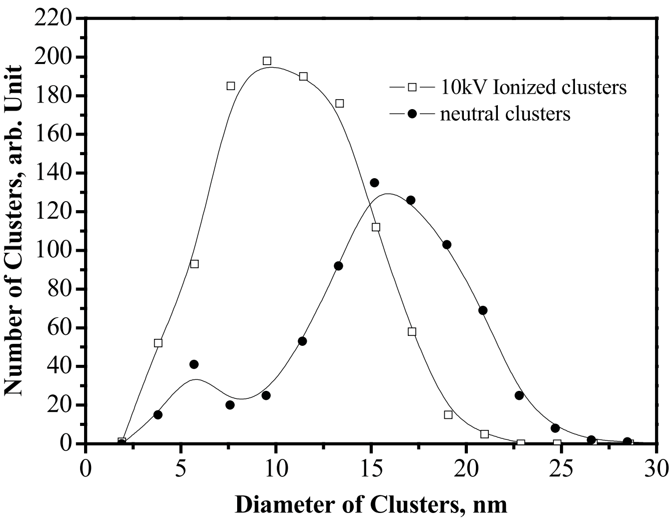

Fig. 3. Size distributions of the clusters deposited from low energy neutral cluster beam and 10 kV ionized cluster beam with normal incidence.

they deposit on the surface. Since the clusters have high mobility on the graphite surface, there are adequately coalescences among the clusters within the diffusion path, so that the observed clusters have spherical morphologies and uniform space distributions. In Figure 2a, the evidence of Oswald ripening (from the areas indicated with circles, where smaller clusters are absorbed by the larger clusters in the center, giving rise to a very large cluster and the vacant space around it) and annealing (from the areas indicated with rectangles, where necks are formed among the adjacent clusters) is widely observed. The morphology has the typical feature of island formation in initial thin film growth from atom deposition. Under energetic deposition, the clusters are mostly pinned on the surface. It is difficult for the clusters to diffuse on the substrate. Coalescences take place locally as a fusion process under cluster-cluster collision with high impact energy. Therefore, the formed cluster assembly has a higher cluster number density, and the shapes of the clusters are more irregular. The morphology of the cluster-based nanostructure has the feature of random deposition.

Under glance incidence, interesting morphology is observed with AFM measurement from the low energy cluster deposits. The shapes of the clusters change from spherical in normal deposition (Fig. 4a) to ellipsoidal in glance deposition (Fig. 4b). The major axes of the clusters are along the cluster incident direction. Due to their initial kinetic energies, the migration of the clusters along the incident direction is enhanced, which induces preferred coalescences in this direction. However, no anisotropic growth evidence is observed from the energetic ionized beam deposition with glance incidence. Clearly, the clusters are also pinned on the surface due to the high impact energy, which overcomes the directional migration.

When the directed cluster beam deposition is performed at glance incidence, if some nano-scale object presents on the substrate, shadow area can be obtained on the substrate at the front side of the object (refer to the beam direction). The shadow area is not directly exposed to the cluster beam due to obstruct of the object so that there is no cluster distribution on it. However, on the front edge of the shadow area, clusters distributed with size and number density gradients can be observed. Figure 5 gives a TEM micrograph of such area for neutral cluster beam deposition at 25° incident angle. The cluster size and number density in the region far from the edge (the upper side of the image) are much smaller than those in the region near the edge. Since the clusters landing on the substrate surface have initial kinetic energies along the incident direction, they will migrate forward preferentially and induce higher cluster number density at the migration front. Therefore a cluster number density gradient is generated near the edge of the shadow area. Such process is conversely equivalent to the gradient induced by diffusion of clusters from the high density region to the vacant region. The cluster number density gradient then generates a gradient on cluster size since the higher the cluster density, the higher the coalescences rate. The effect is equivalent to the size gradient induced by different cluster deposition

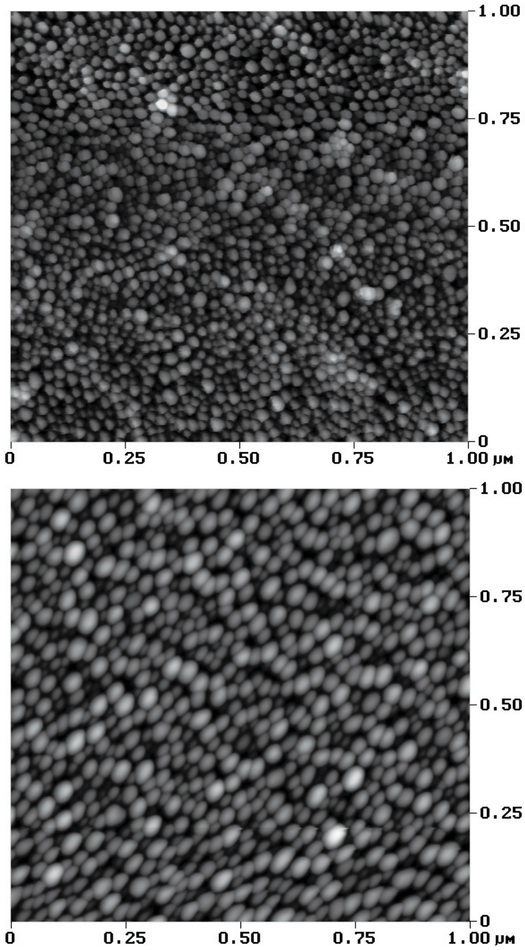

Fig. 4. AFM images of the cluster assembles from low energy cluster beam deposition. (a) Spherical clusters in normal deposition; (b) ellipsoidal clusters in glance deposition.

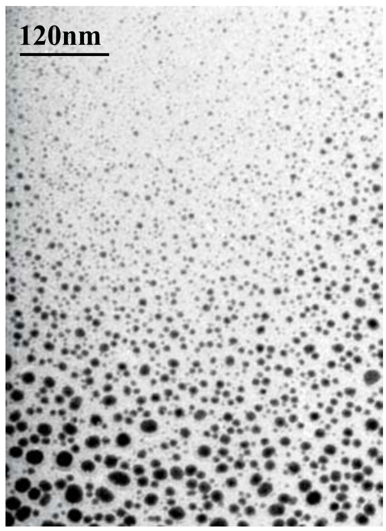

Fig. 5. TEM image of cluster-based nanostructures with number density and size gradient observed at the edge of a shadow area induced by obstructing the cluster beam exposure with a nano-scale object.

rates. Therefore this gradient region shows the process of cluster growth from the initial clusters in the free beam to the final ones in the directly exposed region on the substrate. Owing to the fact that the cluster deposition rate as well as the impacting energy are directly correlated to the incident angle for the high directed beam, the morphology of the deposits as a function of the beam flux, the impact energy of the clusters, as well as the mobility of clusters on the surface can be analyzed based on the TEM observation around the edge of the shadow area. Exactly, we have observed that the length of the gradient region changes with the incident angle of the cluster beam, from $\sim$100 nm at 45° incidence to $\sim\mu$m at 10° incidence. And with energetic cluster beam deposition, the length of the gradient region is much shorter than that with low energy cluster beam deposition, mainly due the pinning of the energetic cluster impacted on the substrate.

4 Conclusion

The morphologies of cluster-based nanostructures from Sn cluster beam deposition are investigated by means of TEM and AFM observation. At normal deposition, the final clusters on the substrate surface have smooth surfaces and spherical shapes. The morphology of the cluster assembly has the typical feature of island formation of initial thin film growth from atom deposition, owing to the high mobility of Sn clusters on the graphite surface. Under energetic deposition, the morphology of the cluster-based nanostructure has the feature of random deposition and the clusters have irregular shapes. Under glance incidence, ellipsoidal clusters with the major axes along the cluster incident direction have been obtained. Cluster distributions with number density and size gradient have been observed at the edge of the shadow area induced by obstructing the cluster beam exposure with a nano-scale object. The mechanism is analyzed based on the initial kinetic energies of the clusters and the migration abilities of the Sn clusters on the graphite surface. It should be pointed that the oblique deposition of the directed cluster beam gives a way to generate nanoparticle arrays with size and number density gradients [8], which may find application in many field.

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