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Optical properties of silicon clusters deposited on the basal plane of graphite

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Abstract

Laser ablation was employed for the deposition of silicon on highly oriented pyrolytic graphite surfaces in an ultra high-vacuum environment that is equipped with Auger electron spectroscopy (AES), scanning tunneling microscopy (STM) and luminescence spectroscopy. For deposition of up to several monolayers, post annealing produced silicon clusters. The size distribution of the clusters was determined as a function of annealing time and temperature using STM. Pure silicon clusters with sizes ranging from 1 to 10 nm showed no detectable photoluminescence in the visible range. Subsequent exposure of these clusters to oxygen at 10^{-6} Torr and for up to 8 hours showed adsorption of oxygen on the surface of the clusters without silicon oxide formation and no detectable luminescence. Hydrogen termination of these clusters was accomplished by exposing them to atomic hydrogen beam but did not result in any detection of the photoluminescence spectra either. Prolonged exposure of these clusters to ambient air, however, resulted in strong photoluminescence spectra with color ranging from red to greenish-blue depending on average cluster size. Auger electron spectra revealed the existence of partially oxidized silicon clusters for these samples. This luminescence could be due to either an oxide phase or to changes in electronic structure of the clusters as a result of quantum confinement effect.

Introduction

Due to its small and indirect band gap, the use of silicon in optical applications is very limited. However, according to the theory of the quantum

confinement effect, when the dimension of a semiconductor is significantly reduced, its electronic energy levels are quantized, which results in an enlargement of the energy gap and a quantization of the electronic density of states [1, 2, 3]. Recent theoretical calculation also predicted a direct gap for surface passivated silicon nanoclusters [4]. Silicon nanoclusters may, therefore, become a promising material for optical applications if their electronic and optical properties are well understood.

In this paper, we show how silicon nanoclusters can be made in a well controlled environment. Surface passivation of these clusters and their optical spectra will then be discussed. Finally, a suggestion for future experiments on these clusters will also be mentioned.

Experimental

In order to have a control over the surface reaction rate which may be important in these small clusters, we proceeded to make them in an ultra-high vacuum chamber (UHV) with a base pressure of $< 5 \times 10^{-10}$ Torr, by laser ablation from a cleaned silicon target onto highly oriented pyrolytic graphite surfaces. The basal plane of graphite was chosen as substrate because all the carbon bonds in this plane are satisfied, and the well known structure of these graphite rings can be used as a calibration for subsequent STM images of the clusters.

Figure 1a shows an Auger spectrum of the as-deposited silicon on graphite. The peak near 270 eV is from the carbon KLL Auger transition. The peak near 90 eV is from the silicon LMM Auger transition. Less than 1% of adsorbed oxygen is seen near 500 eV. Figure 1b shows the Auger spectrum of the same sample after post annealing to 500 C for 5 minutes. Here a reduction in the silicon Auger peak is observed as a result of the formation of bigger silicon clusters (hence reducing the surface area covered by silicon).

Figure 2a shows an STM image of as-deposited silicon on graphite. The as-deposited silicon is observed to have no definite shape and a wide distribution of sizes. After post annealing to 500 C for 5 minutes, a tendency to form aggregations of silicon atoms of average size of 3.0 ± 1.0 nm in diameter is observed (figure 2b). However, as the substrate temperature was raised to 800 C, a surface wetting was evidenced by an increase in the silicon Auger peak (hence increasing the surface area covered by silicon) as shown in figure 3, and by "pancake shape" clusters observed by STM (figure 4). Clusters with pancake shape were expected at this temperature as a result of

bonding of silicon dangling bonds with broken π -bonds in the graphite rings. We were not interested in the clusters with pancake shape, due to its bonding to the graphite substrate and will not discuss any further this type of clusters in this paper.

Photoluminescence was measured *in-situ* with a 15 mW, 325 nm continuous wavelength He-Cd laser, a grating spectrometer and an Oriel Instaspec IV cooled CCD. No detectable photoluminescence from the as-deposited clusters was observed. That could be explained by the fact that on the surface of these spherical clusters, there were dangling bonds and/or surface reconstruction. These surface states have been known to have states in the forbidden gap which quenched the photoluminescence [5,6]. Surface passivation is necessary if these clusters are to be of any use in optical applications.

First, we introduced atomic hydrogen at 10^{-6} Torr into our UHV chamber (by passing molecular hydrogen through a white hot platinum mesh at about 2000 C, with the sample located at about 3 cm behind the mesh), so as to passivate the surface. That did not result in any detectable visible photoluminescence from the clusters.

For many other samples, we carried out surface passivation by flowing oxygen at up to 10^{-6} Torr into the UHV chamber for up to 8 hours. Auger spectra shows adsorption of oxygen on the surface of the clusters without silicon oxide formation. Again, no visible photoluminescence was detected. However, subsequent removal of the samples out of the UHV chamber and ambient air exposure for prolonged period of time (months) resulted in strong photoluminescence spectra with color ranging from red to greenish-blue (figure 5). Auger electron spectra revealed the existence of partially oxidized silicon clusters for these samples (figure 1c).

Spectra similar to figure 5 have also been observed from clusters obtained by ultrasonicing thin sections of anodized porous silicon [7]. These orange-to-blue emission components had shorter lifetimes (several nanoseconds), than the infrared-red emission bands of porous silicon. X-ray photoabsorption measurements on the sample studied in reference [7] showed the presence of only oxidized silicon, suggesting that the shorter wavelength emission components originated from defect centers in an oxide phase. This is also a possible interpretation for the emission spectra in figure 5.

Conclusions

In summary, we have made silicon nanoclusters on the basal plane of graphite. The size distribution and shape of the clusters could be determined as a function of annealing time and temperature. Surface oxidation of these clusters was very difficult to obtain with an oxygen background of pressure up to 10^{-6} Torr. The pristine clusters did not show any visible luminescence, but prolonged exposure of these clusters to ambient air produced strong visible and broad photoluminescence spectra.

At this time, the dominant mechanism for the observed visible and broad photoluminescence spectra from these clusters cannot be clearly determined. *In-situ* surface passivation of these clusters with oxygen at elevated temperature (600 C) and higher background pressure (300 Torr, for example) is carried out in our laboratory. *In-situ* photoluminescence spectra as a function of oxidation time will be obtained and compared with optical absorption spectra (in reflection mode). Efforts to observe the quantization of electronic density of states (if any) of these individual clusters as a function of sizes will also be performed. From these experiments, we expect to tell whether the observed visible photoluminescence spectra from our clusters is a manifestation of the quantum confinement effect or a result of some interfacial luminescence.

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Figure captions

- Figure 1 Auger electron spectra of a) as-deposited silicon on the basal plane of graphite at 5 KeV primary beam energy. The peaks at 92 eV, 272 eV and 503 eV were from silicon LMM, carbon KLL, and oxygen KLL Auger transitions respectively, b) the same sample after post annealing to 500 C for 5 minutes, and c) the same sample after prolonged air exposure. The peaks around 60 eV and 80 eV were from fully and partially oxidized silicon clusters respectively.
- Figure 2 STM images of a) as-deposited silicon on graphite and b) after post annealing to 500 C for 5 minutes.
- Figure 3 Auger electron spectra of a) as-deposited silicon on graphite and b) the same sample after post annealing to 800 C for 5 minutes.
- Figure 4 STM image of a silicon cluster with a pancake shape after post annealing to 800 C for 5 minutes. The horizontal and vertical distances between the two pointers are 2.646 nm and 0.646 nm respectively.
- Figure 5 Photoluminescence spectra of silicon clusters after prolonged air exposure. No STM work has been performed on the silicon clusters in sample 1. Samples 2 and 3 contained clusters with average size of 3 nm and 5 nm (1nm) respectively.

Fig. 1. Auger electron spectra of
a.) as-deposited silicon on graphite;
b.) the same sample after post
annealing to 500 C for 5 minutes;
c.) the same sample after prolonged
air exposure. The peaks around 60 eV
and 80 eV were from fully and partially
oxidized silicon clusters respectively.

a.) As-deposited

b.) Heated to 500 C

Fig. 2. STM image of a.) as-deposited silicon on graphite; b.) the same sample after post annealing to 500 C for 5 minutes.

Fig. 3. Auger electron spectra of
a.) as-deposited silicon on graphite;
b.) the same sample after post
annealing to 800 C for 5 minutes.

Fig. 4. STM image of a cluster with a pancake shape after post annealing to 800 C for 5 minutes. The horiz. and vert. distances between the two pointers are 2.646 nm and 0.646 nm respectively.

Photoluminescence intensity (arb. unit)

Fig. 5. Photoluminescence intensity spectra of silicon clusters after prolonged air exposure. No STM work has been done on sample 1. Samples 2 and 3 contained clusters with average size of 3 nm and 5 nm (± 1 nm) respectively.

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