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## Current Images of CdSe Colloidal Nanodots Observed by Conductive-tip Atomic Force Microscopy

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### ABSTRACT

We have fabricated submonolayer-thick films of CdSe colloidal nanodots in order to investigate electronic properties of individual nanodots by conductive-tip atomic force microscopy (AFM). Topographic and current images of isolated single CdSe colloidal dots on single crystalline Au (111) surface which was covered with dodecanethiol self-assembled monolayer were obtained by AFM operating in contact mode with a conductive tip under appropriate bias voltages. In the current image, it is found that the dot regions have higher electric resistances due to tunneling resistance through the CdSe dots. We also found 10 nm-scale electric inhomogeneity around the dots, which may corresponds to the previously reported etch-pits of Au (111) surfaces formed during the deposition of the dodecanethiol molecules.

### INTRODUCTION

Semiconductor colloidal nanodots have been one of major research interests since they exhibit quantum effect or nano-size effect which is potentially applicable for novel optical and opto-electronic devices [1, 2]. Recently, highly monodisperse II-VI and III-V semiconductor nanodots have been synthesized by colloidal chemical techniques [3, 4]. Because they are free from the lattice mismatched substrate, the choice of materials for colloidal dots is wider than that for self-assembled quantum dots formed by Stranski-Krastanov mode growth by molecular beam epitaxy or metal organic chemical vapor deposition. The optical properties of the colloidal dots have been widely investigated, and it has been recognized that the surface termination may be playing an important role for the properties. We have reported an optical memory effect of CdSe colloidal nanodots

where the photoluminescence (PL) intensity of the nanodots spun-coat on glass substrates depends on the photoexcitation energy and duration [5]. This effect is strongly influenced by the preparation process of the sample, and the main contribution is therefore attributed to electron trap states at the interface between the CdSe nano crystals and organic molecules covering them.

In order to study the interface properties of colloidal nanodots, electronic investigation have advantages over optical since interface traps are known to be non-radiative. We thus adapted conductive-tip atomic force microscopy (AFM) [6, 7] for nano scale electronic study of CdSe colloidal nanodots. In this paper, we report on fabrication of sub-monolayer thick CdSe colloidal nanodot film for electronic investigation of individual nanodots, and observation of current images of single CdSe colloidal nanodots as well as substrate surfaces.

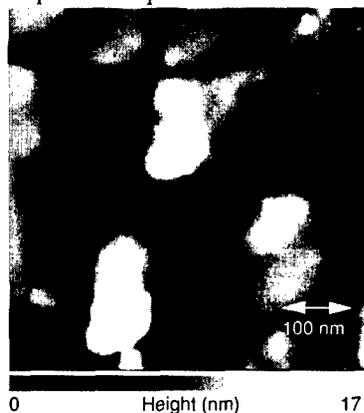
## EXPERIMENT

The CdSe colloidal nanodots were synthesized by injecting precursor that contains Se dissolved in tributylphosphine and dimethyl cadmium into tri-*n*-octylphosphine oxide (TOPO) at temperatures ranging from 300 to 350 °C. Here, the TOPO not only act as hot soap where nucleation and growth occur but also caps and passivates the CdSe nanodot surfaces. The obtained nanodots were dispersed in toluene, and coated on substrates using a spinner at 3000 rpm for 30 sec. The average diameter of the nanodots and its distribution is estimated to be 5 nm and 10-20 %, respectively, from optical absorption measurements.

The morphology of the sample surface were measured using a high vacuum AFM system operating in contact mode, and local electric current was simultaneously mapped by applying an appropriate bias voltage between the sample and conductive tip.

## RESULTS AND DISCUSSIONS

In order to investigate the electric properties of the individual CdSe colloidal nanodot by AFM, we need submonolayer-thick nanodot films where isolated nanodots exist on the substrate surface. Because the TOPO

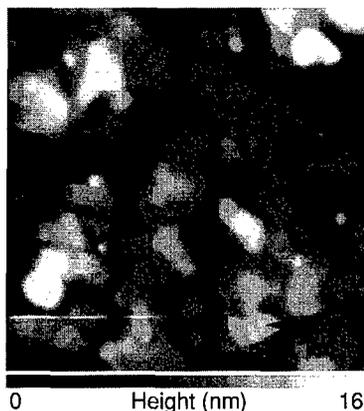


*Figure 1. Topographic image of CdSe colloidal nanodots spun-coat on a Si wafer*

molecules covering the CdSe nanodot surfaces are hydrophobic, the substrates with hydrophilic surfaces are not appropriate for preparing submonolayer-thick films.

Figure 1 shows an AFM image of a silicon wafer on which toluene solution containing 0.1 wt% CdSe colloidal dots is spuncoat. It is seen that single nanodots do not exist, and instead, 100 nm-scale islands which seem to consist of aggregated colloidal dots are formed, prevailing that this sample is not suitable for our purpose.

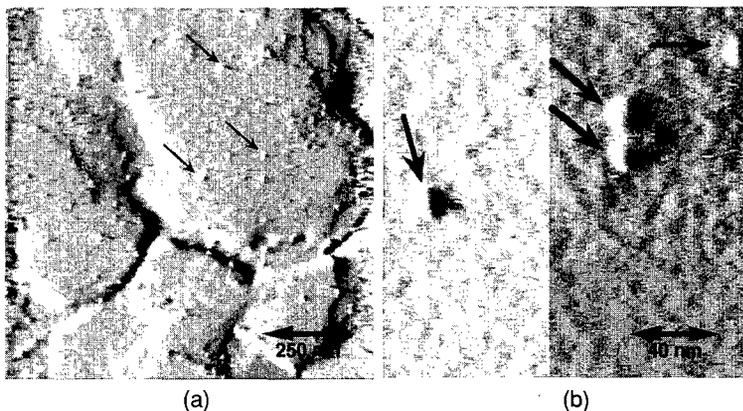
We therefore tried to prepare a substrate with hydrophobic surface. One promising candidate was gold films on which alkanethiol self-assembled monolayer (SAM) was formed, where the sulfur atom at one end of alkane chain forms a chemical bond with gold, and the alkane chains are aligned perpendicular to the gold film surface. Figure 2 shows a contact mode AFM image of Au (111) single crystalline film formed on a mica substrate by vacuum evaporation. Note that the film



**Figure 2.** An AFM image of Au (111) single crystalline prepared on mica

consists of sub-micron size single crystals, and the (111) surface of each crystal is so flat that single nanodots, if they are on the surface, can be easily distinguished.

After forming dodecanethiol SAM on the Au (111) surface by dipping the sample in 1 mM dodecanethiol ethanol solution for 3 hours, 0.1 wt% CdSe colloidal dots in toluene solution was spun-coat under the same conditions as on the silicon substrate. The

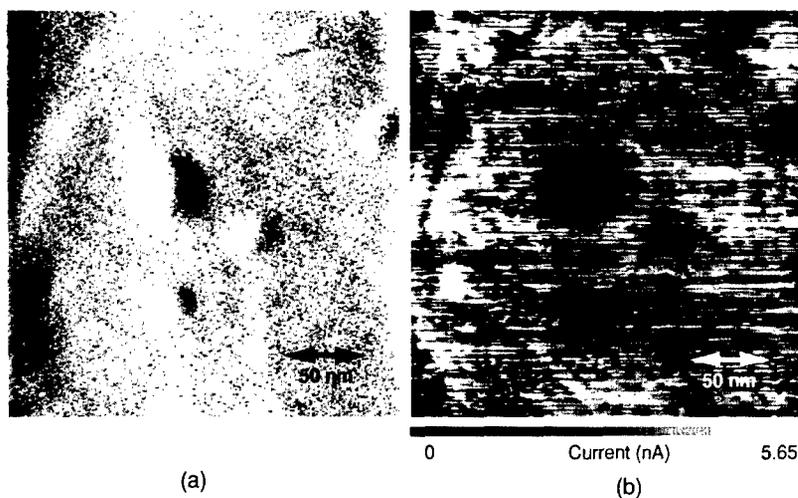


**Figure 3.** Single CeSe colloidal nanodots on Au (111) surface which is covered with dodecanethiol SAM: (a) low and (b) high magnification images by AFM.

differential image of the sample by contact-AFM is shown in Fig. 3 (a) and (b). In the former image, we can see that single nanodots are scattered on the Au (111) surfaces as some of them are indicated by arrows. In the latter, four single dots of about 20 nm-diameter are observed. The apparent diameter is larger than that estimated from the optical absorption measurement. We attribute this discrepancy to the large radius of the AFM tip since a 40 nm-thick metal layer is evaporated on the tip in order to ensure conductivity.

Then, we simultaneously imaged surface topography and local electric current by applying a bias voltage of 1.0 V. Figure 4 (a) is a differential image taken by contact-AFM. The three protuberances of nearly 30 nm-diameter are single nanodots as in Fig. 3 (b), and the large one near the center of the image may consist of a few dots that are aggregated. Comparing the topographic and current images, it is found that the protuberant region has larger electric resistance. Namely, the dots exhibit larger resistance since the tunneling resistance of the CdSe dots is added to that of the dodecanethiol SAM.

We can also see nm-scale electric inhomogeneity all over the substrate surface in the current image. If the substrate surface is not homogeneous on this scale, it would prohibit us from an electronic measurement of individual colloidal dots. However, it has been reported that a few nm-diameter holes of 0.3 nm depth, which are called etch-pits and observed by scanning tunneling microscopy (STM), exist on the Au (111) surfaces covered with alkanethiol SAM [8]. They are believed to be formed as a result that occurs the surface reconstruction changes during the deposition of alkanethiol SAM. We also observed those etch-pits on our substrate surface by STM, and confirmed that their depth



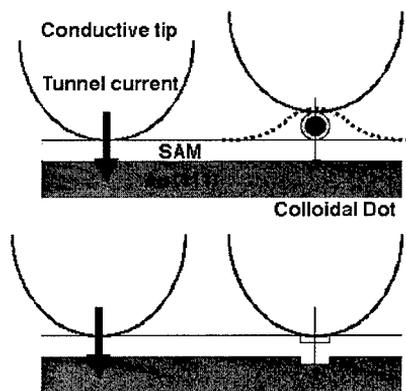
**Figure 4.** Simultaneously measured (a) differential topographic image and (b) current image of CdSe colloidal nanodots by AFM

was 0.3 nm. Thus, the inhomogeneous structures in the current image correspond to the etch pits.

A model that explains the correlation between the topographic and current images of our sample is described in Fig. 5. The conductive AFM tip used in our measurements has a much larger radius than that of STM tips as discussed earlier. Thus, single colloidal nanodots of about 5 nm-diameter appears as a few tens nm in both the topographic and current images. In the topographic image, however, the etch-pits are not observed because the size of the etch-pits is smaller than the resolution that can be reached with AFM tip that is employed. On the other hand, tunneling current decreases when the AFM tip is scanned over the etch-pits since the tunneling gap increases by 0.3 nm.

## CONCLUSIONS

We have fabricated submonolayer-thick CdSe colloidal nanodot films on alkanethiol SAM on single crystalline Au (111) surfaces in order to investigate electronic properties of individual nanodots. Topographic and current images of the sample were successfully obtained simultaneously using a conductive-tip AFM. In the current image, the dot region has larger electric resistance due to tunneling through the dot. We have also observed nm-scale electric inhomogeneity found on the surface that corresponds to etch-pits formed by deposition of SAM on the gold surface.



**Figure 5.** A model explains the topographic and current images of single CdSe colloidal nanodots on Au (111) covered with dodecanethiol SAM

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