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74

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PREPARATION OF SAMPLE FOR STM LUMINESCENCE SPECTROSCOPY OF SINGLE SiC NANOCRYSTAL USING CT PROBE

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We aim at characterizing luminescence from nanometer-scale crystalline SiC volumes embedded on the crystalline Si surface by cathode luminescence and photo luminescence measurement methods with high-spacial resolution using a conductive transparent (CT) probe. The CT probe can inject electrons or photons for excitation in the same nanometer area, and detect weak luminescence with high efficiency. In order to observe STM luminescence spectroscopy using the CT probe, we prepared samples of nanoscale crystalline SiC volumes at the SiO_2/Si interface, by annealing SiO_2/Si substrate structures for various times in 200 mbar CO gas ambient pressure at 1100°C. It is found that the shorter the annealing time is, the smaller the size of nanocrystal is. We were able to synthesize the ideal sample having SiC nanocrystals within 10 nm in diameter on the Si surface by annealing for 30 minutes.

I. Introduction

Materials with atomic and nanometer size make it possible to show new properties derived from a quantum effect, which cannot be exhibited in the bulk structure. Therefore, many researchers have expected and investigated new functions appearing in the nanostructures so far. The structure difference in the atomic level of individual nanoparticles causes a large energy shift in the electronic structure by an electron confinement effect in nanometer volume. The large energy shift should be necessarily reflected to the energy shift and the intensity of the photoemission spectrum. As a result, the characterization of luminescence from the nanometer volume is important to understand the property of nanomaterials.

Electron-hole pairs production regarding the luminescence are generated by electron or light injection and excitation. Due to the difference of the basic properties between electron and photon such as electric charge, momentum, and propagation characteristics, the obtained information is quite different in the cathode luminescence (CL) and the photo luminescence (PL) phenomena. Therefore, the complementary evaluations of nanomaterials by the CL and the PL methods are useful to completely investigate both electronic and optical properties of themselves. In the ordinary scanning tunneling microscope (STM) system and near field scanning optical microscope (NSOM) system, however, we cannot measure electronic and optical properties as well as the atomic configuration simultaneously at the same position and the same period time.

In order to overcome these problems, a new scanning probe microscopy was designed and developed by Murashita *et al*. [1, 2]. In this new microscopy, electrons or photons can be injected into the sample through a conductive transparent (CT) probe in the same nanoscale area, and very weak luminescence can be detected with high efficiency due to the large solid angle of detector. The typical structure of the CT probe

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is schematically depicted in Fig. 1.

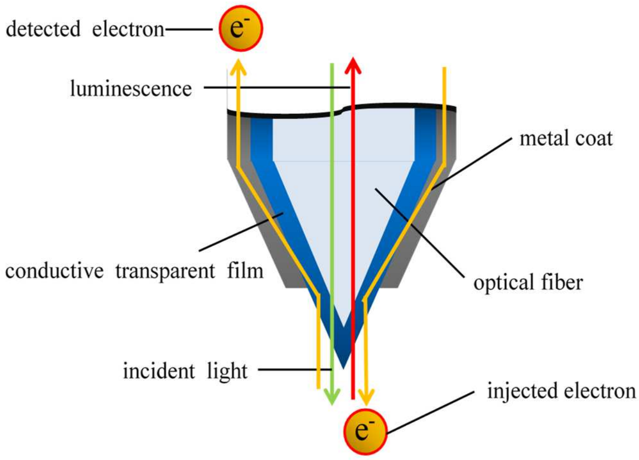

Fig. 1. Schematic image of CT probe. The inner optical fiber transmits light and the outer metal part transports electrons through conductive transparent film

In this study, we aim to evaluate luminescence from the nanometer-scale crystalline SiC volumes exposed on the crystalline Si substrate surface, using STM luminescence spectroscopy by tip excitation and tip concentration of light using the CT probe. The STM luminescence spectroscopy is a method to detect luminescence emitted when the electrons excited by injection of tunneling-electron from the tip to the sample recombine with holes. Fig. 2 shows the process of tunneling-electron luminescence.

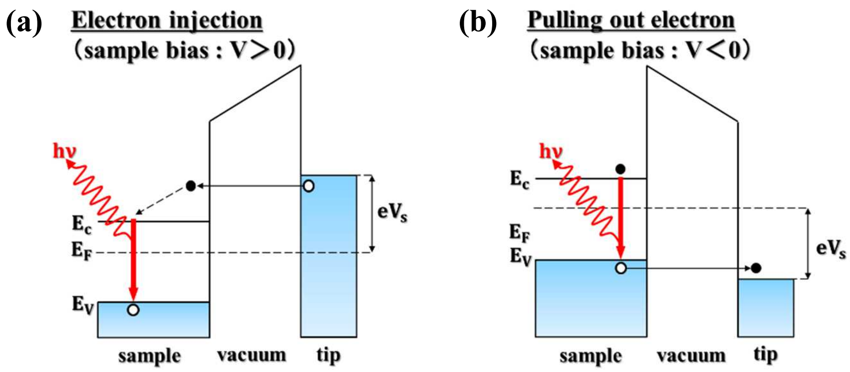

Fig. 2. Process of tunneling-electron luminescence. (a) Luminescence from recombination of the electron injected from the tip to the sample. (b) Luminescence from recombination of the hole generated by pulling out the electron from the valence band of the sample to the tip.

This method, which has special features of small tunneling-electron beam diameter and variable injection energy, can inject and pull out tunneling-electrons. We prepared SiC nanocrystals on the crystalline Si substrate as the standard sample emitting light from the nanometer area. Since SiC is indirect transition type semiconductor, its light emitting probability is extremely low in the bulk structures. Three-dimensional carrier confinement by forming SiC nanocrystals within 10 nm in diameter, however, makes the emitting light probability increasing. This is because the band structure and the dipole selection rule are significantly changed, resulting in the increase in the recombination probability of electrons and holes. Since the emission wavelength of semiconductor nanocrystals varies with size, it is important to evaluate size and optical property at the atomic level and at the same point of sample. It is required that SiC nanosrystals within 10 nm in diameter are exposed on the surface and are not too dense, in order to individually measure the luminescence from a single nanocrystal by the STM luminescence spectroscopy using the CT probe.

II. Experimental

Fig. 3 shows the formation process of SiC nanocrystals on the Si substrate. We prepared thermally grown SiO_2 films with 150 nm thick on the Si(100) substrates by oxidation in dry O_2 ambient under 1 atm at 1000°C for 3 h. CO diffusion to the interface was performed in 200 mbar CO pressure at 1100°C for various times of 2 h, 1 h and 30 min. SiC nanocrystals are known to be formed at the SiO_2/Si interface because of CO diffusion through the SiO_2 layer and reaction with the interfacial Si by annealing. Since the nucleation density of SiC nanocrystals depends on the CO pressure, we decided CO pressure so that the density of nanocrystals does not become too large [3]. Surface morphology was observed by atomic force microscopy (AFM) after we have removed the SiO_2 layer by HF treatment.

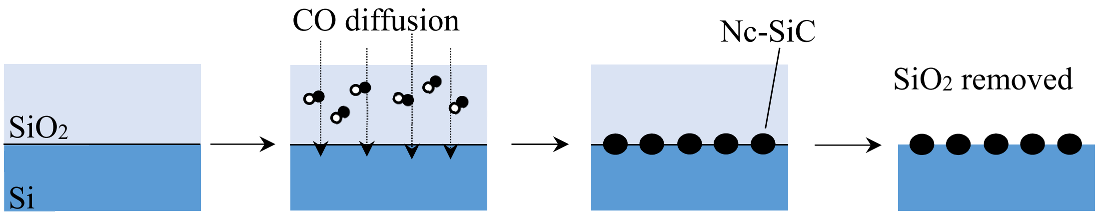

Fig. 3. Formation process of SiC nanocrystals on the Si substrate.

III. Results and Discussion

Fig. 4 shows the AFM images and the cross-sectional shapes of the samples with different annealing time. The single SiC nanocrystal shown by the cross-sectional shape is lined. The nucleation density of SiC nanocrystal is 1.0×10^{10} cm^{-2} regardless of annealing time. This value is sufficiently small for evaluation of the individual nanocrystals. The nanocrystal diameter of samples annealed for 2 h, 1 h and 30 min are 30 nm, 15 nm and 10 nm respectively, and thus it is found that the shorter the annealing time is, the smaller the size of nanocrystal is. The quantum size effect becomes remarkable when the semiconductor nanocrystal is 10 nm or less in diameter, so that the semiconductor nanocrystal emits light. Therefore, the annealing for 30 min is optimum as preparation condition of sample for STM luminescence spectroscopy.

It is found that nanocrystals grow randomly since the sizes of the SiC nanocrystals annealed for longer period become larger. In addition, the fact of the nucleation density does not vary regardless of the annealing time shows that the growth process of nanocrystals becomes dominant after the short nucleation process.

The nanocrystals of each sample have characteristic shape surrounded by pits. These pits are caused by forming SiOx with SiC according to the following reaction:

$$2CO + 3Si \rightarrow 2SiC + SiO_2,$$

after CO diffuses in SiO_2 without dissociating and dissociates at the SiO_2/Si interface.

Then, the pits are formed after removing thermal oxide and SiOx with HF.

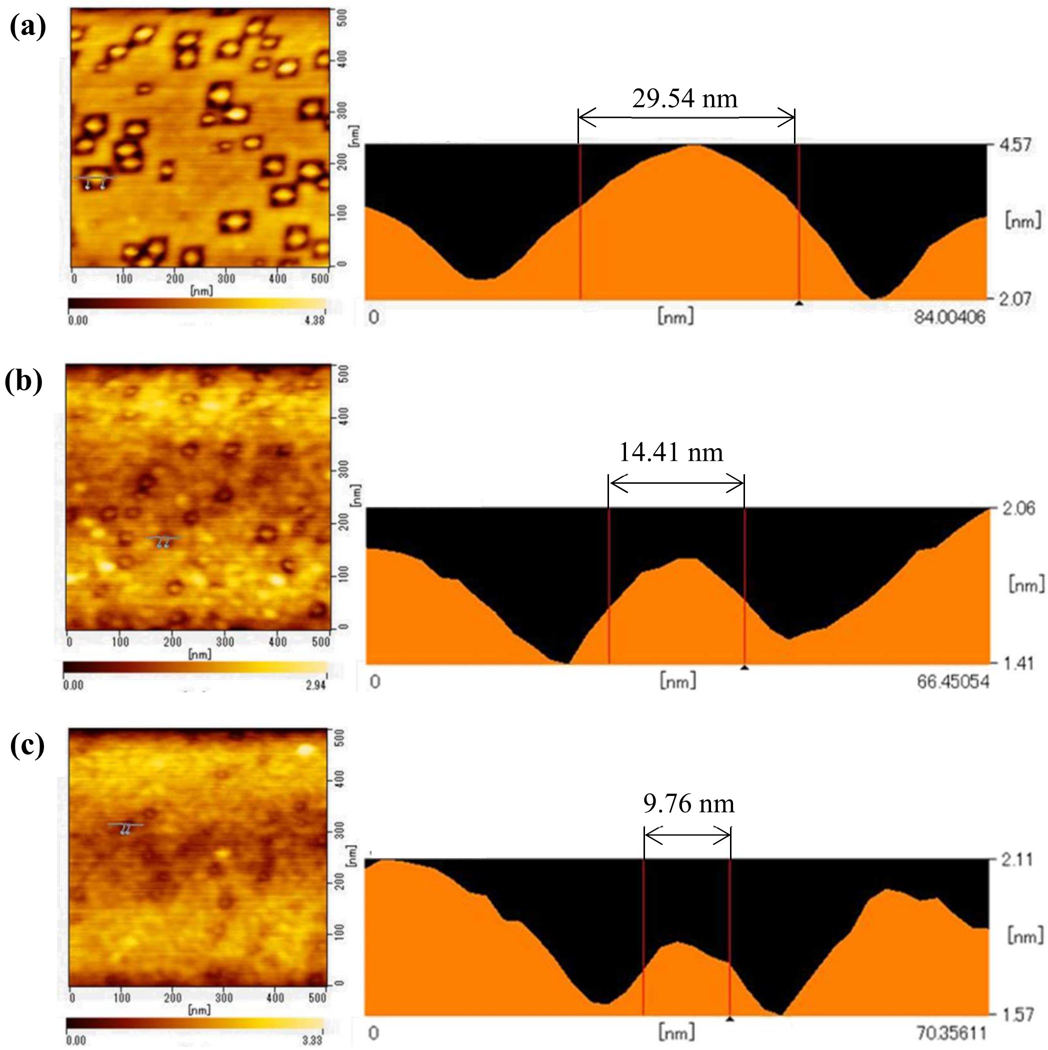

Fig. 4. The AFM images and the cross-sectional shapes of the samples with different annealing time. (a)2 h, (b)1 h, (c)30 min

IV. Conclusions

We were able to prepare the ideal sample having SiC nanocrystals within 10 nm in diameter exposed on the surface by annealing the SiO_2/Si substrate in 200 mbar CO ambient pressure at 1100°C for 30 min and by removing SiO_2 film with HF. We measured the diameters of SiC nanocrystals with AFM. Further, we would evaluate the exact sizes using STM, and optimize sample synthesis conditions. In addition, we plan to obtain STM luminescence spectra of the single SiC nanocrystals using the CT probe in the near future.

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