Photoluminescence and TEM studies of self-limiting oxidation of nanocrystalline silicon dots

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Reducing the size of Si nanostructures to sub-5 nm is an important task to improve the electrical and optical properties of present Si nanostructures. By employing the oxidation, the diameter of the nanocrystalline silicon (nc-Si) dot core decreases with the oxidation time increases, which is observed by TEM and photoluminescence (PL). However, the diameter reduction of the core is retarded when the diameter of the core reaches a value, which is determined by the initial diameter. A preliminary model suggests that the increased stress normal to the Si/oxide interface decreases a reaction rate constant at the interface. The stress is a result of viscous flow of the oxide when the new oxide is formed. The strong stress let the reaction rate constant be nearly zero and the core still remains against the long-term oxidation.

I. Introduction

We have successfully fabricated nanocrystalline silicon (nc-Si) dots with diameter of 8±1 nm [1], which shows single electron effect at low temperatures [2]. For room temperature operation of quantum effect devices, however, further reduction of dot size is required. On the other hand, recent interest in exploring the optical properties of Si nanostructures has intensified the search for a reliable technique in fabricating sub-5 nm Si structures [3]. Earlier work on the oxidation of nonplanar Si structures indicates that the oxidation rate decreases with decreasing structural dimensions (self-limiting oxidation) because of the associated compressive stress normal to the Si/oxide interface caused by the volume difference between Si and SiO_2 [4,5].

In this work, we have achieved sub-5 nm Si structures by reducing the size of the present nc-Si dots with a good reproducibility using the self-limiting oxidation. Simultaneously, a photoluminescence (PL) property related to the self-limiting oxidation is observed.

II. Experimental

The Pt meshes were used as the substrates for TEM observation and the Si (100) were used for PL measurements. Nc-Si dots were deposited on the substrates by VHF PECVD. The Si (111) lattice image of high resolution TEM (Fig. 1) indicates that nc-Si dot grown by the process is a single crystal. The core of the nc-Si dot is covered with the amorphous oxide layer. The detailed deposition procedures of the nc-Si dot have already been given in Ref. 6. After the deposition of the nc-Si dots, all samples were thermally oxidized in dry O_2 atmosphere at 750-850 ˚C for 0-15 hour. The diameter of the nc-Si dot core was observed by TEM. PL measurements were performed at room temperature using the 325 nm line of the He-Cd laser as an excitation source.

III. TEM Observation

The variation of the diameter of the nc-Si dot core with oxidation is deduced from TEM images. TEM images of the surface oxidized nc-Si dots at 750 ˚C for 1 hour and 15 hours are shown in Fig. 1(a) and (b), respectively. By employing the oxidation, the diameter of the nc-Si dot core decreases and the thickness of the oxide layer around the core increases. The diameter of the nc-Si dot cores is plotted as a function of the oxidation time at the oxidation temperatures of 750 ˚C and 850 ˚C in Fig. 2. In the initial stages of the oxidation, the diameter of the core reduced rapidly at all the oxidation temperatures for all the initial diameters. After the initial oxidation, the diameter of the core is hardly changed at the oxidation temperature of
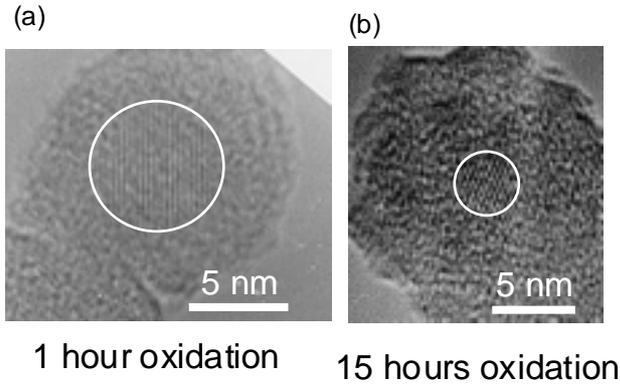
Figure 1:TEM images of one of the nc-Si dots oxidized for (a) 1 hour and (b) 15 hour at 750 °C.

Figure 2: Diameter of the nc-Si dot core plotted as a function of the oxidation period.

750 °C despite of the long-term oxidation. In the case of the initial diameter of 9.4 nm, the diameter of the core is ~4 nm after 15 hours oxidation although the diameter reaches at ~5 nm for 6 hours oxidation. However, in the case of 850 °C, the core is not observed by TEM for a longer oxidation period, which is depended on the initial diameter.

IV. PL Measurements

The PL spectra of the surface oxidized nc-Si dots at 750 °C for 10 minutes and 8 hours are illustrated in Fig. 3(a) and (b), respectively. An emission peak is observed in each PL spectrum, which can be decomposed into two Gaussian curves (denoted as P1 and P2 in Fig. 3). P1 and P2 are related to the nc-Si dots because these emissions are not observed in the Si and quartz substrate. The center energy of P2 shows a blueshift of ~300 meV throughout the oxidation while that of the P1 shows a blueshift of ~40 meV. Center energy of P2 is plotted as a function of oxidation time at the oxidation temperatures ranging from 750 °C to 850 °C in Fig. 4. In the initial stages of the oxidation, the center energy of P2 shows rapid blueshift (240 meV/hour at 750 °C and 500 meV/hour at 850 °C). However, the slope of the blueshift is ~10 meV/hour for all the oxidation tempratures after the initial oxidation. In some PL spectra, the

redshift of the P2 is observed between the rapid and the slow blueshift.

V. Discussion

The widely accepted model of the one-dimensional thermal oxidation of Si is based on the Deal-Grove model [7]. The physical mechanism is the diffusion of oxidants through the existing oxide to react with the Si to form a new oxide at the Si/oxide interface. D.B. Kao *et al*. have successfully expanded the one-dimensional Deal-Grove model to the two-dimensional model of the Si cylindrical structure [4,5].

Although a shape of the nc-Si dot is a three-dimensional sphere, the oxidation of the nc-Si dot is not quantitatively explained by the expanded Deal-Grove model. However, it is possible to discuss the oxidation of the nc-Si dot, qualitatively.

By employing the oxidation of the nc-Si dot, two types of stress is generated, which are a result of viscous flow of oxide when new oxide is formed. In the expanded Deal-Grove mode, a stress normal to the Si/oxide interface σ play an important role to retard the oxidation rate of the nc-Si dot. The stress normal to the interface is given by
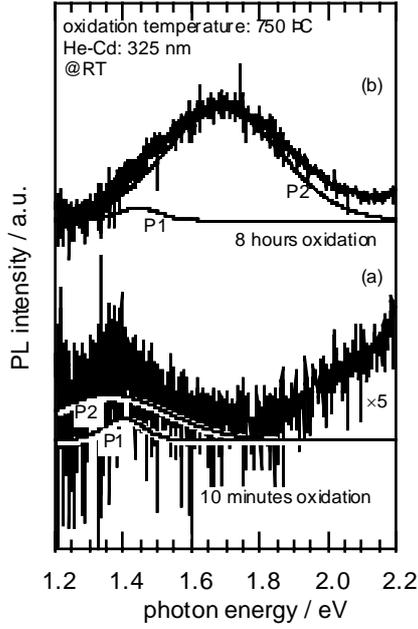
Figure 3: PL spectra of the nc-Si dot oxidized for (a)10 minutes and (b) 15 hours at 750 °C.

Figure 4: Center energies of P2 plotted as a function of the oxidation period.

$$\sigma = 2\eta\xi\left(1/a^2 - 1/b^2\right), \qquad (1)$$

where η is the viscosity and ξ the velocity constant to be determined from the oxide growth rate at the interface. The stress affects the reaction rate constant k_s, which is given by

$$k_s = k_0 \exp\left\{-\sigma\left(\Omega_{SiO_2} - \Omega_{Si}\right)/kT\right\}, \quad (2)$$

where $\Omega_{SiO2} = 45$ Å^3 is the molecular volume of SiO$_2$, $\Omega_{Si} = 20$ Å^3 is the atomic volume of Si, and k_0 is the stress-free value of k_s.

To simplify the problem, the values of η and ξ are assumed to be independent of a and b although η is a function of a tensile stress P. A value of $(1/a^2-1/b^2)$, which is in proportion to the stress normal to the interface from Eq. (1), is plotted as a function of Δa for the various initial nc-Si dot core diameters in Fig. 5(b). The value of $(1/a^2-1/b^2)$ is low when Δa is small, indicating that the stress normal to the interface is low at the initial oxidation. The value of $(1/a^2-1/b^2)$ rapidly increases when Δa is near the initial diameter a_0, indicating that the stress increases rapidly. According to Eq. (1) and (2) and Fig. 5(b), a value of the reaction rate constant is small when Δa is near a_0. As a result, the oxidation rate of the core decreases and the core still remains against the longer oxidation period.

According to the Eq. (2), the reaction rate

constant is high despite of the same value of the stress normal to the interface when the oxidation temperature T is high. The oxidation rate is enhanced at the high oxidation temperature. The reducing rate of the core at 850 °C is higher than that at 750 °C (Fig. 2).

Although the surface oxidized nc-Si dot fabricated by VHF PECVD show PL, which is similar to porous Si and Si nanostructures, the mechanism of visible luminescence from the nc-Si dot is still controversial. Kanemitsu et al. proposed that the origin of the 1.65 eV PL band is a radiative recombination of the excitons localized at the interface between crystalline Si core and the surrounding SiO$_x$ layer in the case of the surface oxidized nc-Si dot [8]. When the size of nc-Si dot is smaller than the exciton Bohr radius of ~5 nm and the bandgap energy of the core is larger than that of the interface state, excitons are localized near the disordered interface between core and the surrounding SiO$_x$ [8]. Because the behavior of the center energy of P2 at the oxidation temperature of 750 °C against the oxidation time (Fig. 4) is similar to the behavior of the core diameter measured by TEM (Fig. 2), the P2 can be described by a localized exciton emission mode. The center energy of P2 can be affected by the quantum confinement and the stress.

The observed blueshift of P2 (Fig. 4) is explained by the enhancement of the quantum confinement due to the size reduction of the core. It is interesting to note the redshift of P2
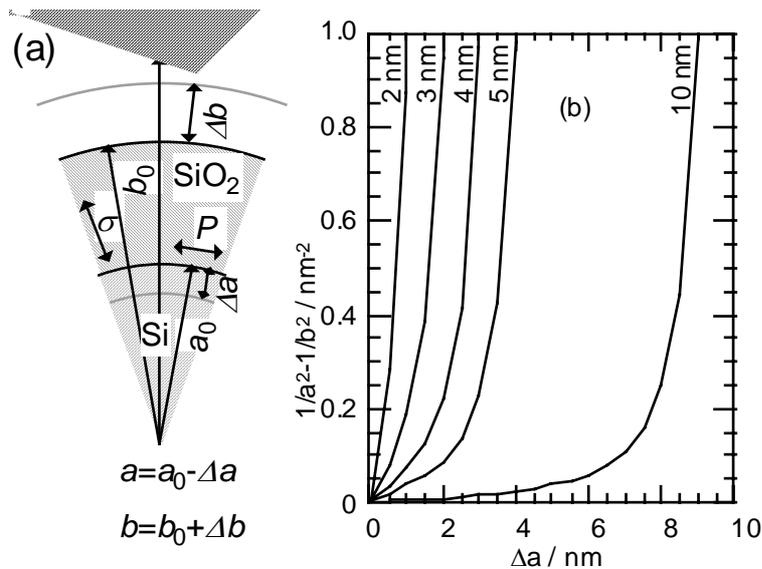
Figure 5: (a) The structure of nc-Si dot used in the oxidation model. a_0 and b_0 are the radius of the Si core and oxide at the initial state, respectively. Δa and Δb represent a difference from their initial value of a_0 and b_0, respectively. σ and P represent the stress normal to the interface and the tensile stress in the surrounding oxide layer, respectively. (b) $1/a^2 - 1/b^2$ plotted as a function of Δa for the various initial core diameters.

between 2 and 4 hour. A possible account is the compressive stress to the nc-Si cores if the band transition of the nc-Si dots is the indirect one, since the pressure coefficient of the bulk crystalline Si is about –1.4 meV/kbar [9] for the indirect gap and 5.2 meV/kbar [10] for the direct gap, whereas amorphous Si:H is about –2meV/kabr [11].

VI. Conclusions

Oxidation of the nc-Si dots has been investigated by TEM and PL. While the diameter of the nc-Si dot core decreases rapidly in the initial stages of the oxidation, the core remains after the prolonged oxidation. The increased stress in the surrounding oxide layer caused by the volume difference between Si and the oxide retards the reaction rate constant at the Si/oxide interface. The oxidation at the interface is repressed due to a small value of the reaction rate constant.

Acknowledgements

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Comparing Fig. 2 and Fig. 4, the behaviour of the core diameter against the oxidation time is similar to that of the center energy of P2. L. Patrone et al. have found the relationship between the emission peak energy of the sphere shape nc-Si dot prepared by the laser ablation method and the diametr of the nc-Si dot, experimentally, as follows,

$$E_g = 1.17 + 3.283d^{-1.34}. \qquad (5)$$

Because the shape of the nc-Si dot prepared in this study is a sphere, the diameter of the core will be drawn by Eq. (*). The right axis of Fig. 4 is obeyed by Eq. (*). The diameter of the core reduced rapidly in the initial stages of the oxidation, followed by the slow reduction of the core after the initial oxidaiton, which is the same result observed by TEM.

High-pressure physics predicts that viscosity should have the opposite temperature and pressure dependence. The relationship of viscosity under pressure in Eq. (*) is reported by Dane and Birch and applied in this model.

$$\eta = \eta_0 \exp(-\alpha \times P), \qquad (4)$$

where η_0 is the viscosity at zero pressure, and α is an empirical parameter. The viscosity at zero pressure is generally estimated as a function of temperature and the value decreases with high temperature.
The value of $1/b^2$ is plotted as a function of Δa for the various initial nc-Si core diameters in Fig. 5(c). The values of η and ξ are assumed to be independent of a and b although η is a function of P. The value of $1/b^2$ is high when Δa is small, indicating that the tensile stress P is high at the initial oxidation. The value of $1/b^2$ decreases when Δa is near the initial diameter,

indicating that the tensile stress decreases.

In that model, the surface reaction coefficient k_s is reduced by the normal viscous stress at the Si/oxide interface. Under a normal stress, the volume expansion necessary to form a new oxide must be achieved against the stress. The simplest way to incorporate the stress effect is to add to activation energy the additional work that must be carried out by the expanding new oxide.

In the expanded Deal-Grove model, it is predicted that the retardation of the oxidation rate of nc-Si dots is caused by the stress induced near Si/oxide interface. There are two types of stress that can affect the oxidation rate. These stresses are a result of viscous flow of oxide when the new oxide is formed. One is the tensile stress P generated in the oxide, another is the normal stress σ generated at Si/oxide interface, as depicted in the inset of Fig.5(a).