RETARDATION IN THE OXIDATION RATE OF NANOCRYSTALLINE SILICON QUANTUM DOTS

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ABSTRACT

Using very-high-frequency (VHF) plasma decomposition of SiH₄ and pulsed gas technique, we have successfully prepared nanocrystalline silicon (nc-Si) quantum dots having average diameter of 8 nm and dispersion of 1 nm. The role of natural oxide is very important. It controls the size of nc-Si dots. Of particular interest is that the oxidation of these dots can be self limited, due to the stress induced near Si/oxide interface, which would allow further reduction of size and improvement in dispersion. This paper deals with the systematic study of oxidation process of nc-Si dots. Nc-Si dots formed in an Ar plasma with SiH₄ gas pulses are deposited onto a Pt mesh. The dots are then oxidized at 750, 800 and 850°C from 20 minutes to 15 hours. The dimensions of the residual nc-Si and the grown oxide are measured directly from the TEM micrographs and analyzed. For comparison, field oxide is investigated using ellipsometry. Retardation in the oxidation rate of nc-Si is observed. The mechanism of the reduction of oxidation rate in nc-Si is discussed taking into account the effect of stress.

INTRODUCTION

In future quantum effect devices, e.g., single electron transistors and single electron memories, small conducting islands will be major components. When these devices are to be operated at room temperature, nc-Si dots are required to have a diameter of less than 5 nm. Using very-high-frequency (VHF) plasma decomposition of SiH₄ and pulsed gas technique, we have successfully prepared nanocrystalline silicon (nc-Si) quantum dots with an average diameter of 8 nm and dispersion of 1 nm[1],[2]. Recently, it is reported that the oxidation rate of lithographically patterned Si columns (Si nanocolumns) is retarded by the stress induced near Si/oxide interface[3],[4]. Moreover, in Si nanocolumns, the self-limiting effect of oxidation is observed. In principle these same effects should be observed for nc-Si dots, which would allow the control of nc-Si dot size with a small dispersion.

EXPERIMENT

Nc-Si dots are deposited onto a Pt mesh for simple TEM sample preparation. Before deposition, the Pt mesh is coated by a CVD derived SiO₂ film to prevent nc-Si from reacting Pt mesh. After coating, Pt mesh is annealed in O₂ atmosphere at 900°C to remove C, OH⁻ and other impurities. A schematic diagram of nc-Si deposition system is shown in Figure.1. The electrodes of plasma cell are capacitively coupled. The stainless steel plate with an orifice of 6 mm diameter and 2 mm length, separating the UHV chamber from the plasma cell, is used as the grounded electrode. The deposition rate is monitored by a quartz crystal sensor during deposition. The
pressure in the cell is monitored by a capacitance manometer and is controlled by the flow rate of gases. The flow rate of gas is controlled by a mass flow controller and computer controlled air valve. Nc-Si is fabricated by coalescence of radicals from SiH₄ plasma in plasma cell and extracted from plasma cell to the UHV chamber through the orifice. Nc-Si dots are deposited onto the Pt mesh.

After the deposition, nc-Si and Si(100) substrate are oxidized for various periods at temperature of 750, 800, 850°C in a tube furnace. Nc-Si size is directly observed by using TEM. Figure 2 shows the high-resolution TEM micrographs of nc-Si dots. The Si(111) lattice image indicates that nc-Si grown by the process is a single crystal. The amorphous layer covering the nc-Si in Figure 2(a) is natural oxide formed by the exposure to ambient atmosphere.

RESULTS

The oxide thickness and the diameter of residual nc-Si are extracted from micrographs and analyzed. Figure 3 shows the oxide thickness and the diameter of residual nc-Si when nc-Si is oxidized at 750 and 850°C. For comparison, the thickness of thermal on Si(100) wafer under identical conditions is investigated using ellipsometry. The values in the legends of the graphs are the initial diameter of nc-Si, which is calculated from the Si molar volume of the measured oxide thickness which is added to the diameter of residual nc-Si dot. In Figure 3(a), (c), the

![Figure 1 Nc-Si deposition system](image)

![Figure 2 TEM micrograph](image)

F5.3.2
The oxidation rate of nc-Si is significantly retarded as compared with Si(100) substrate. Nc-Si dots remain even for prolonged oxidation at 750°C as shown in Figure 3(b). At 850°C, the nc-Si with initial 20 nm diameter can be observed after 4 hours of oxidation. However, in case of an initial 10 nm dot, we cannot observe crystalline Si after 1 hour of oxidation. Therefore, the self-limiting effect is dependent on the oxidation temperature and particle size.

**DISCUSSION**

To discuss the retardation of oxidation rate, we can apply the modified Saraswat’s oxidation model [5] for nc-Si. Deal-Grove’s oxidation model [6] is used for Si(100) substrate. The Saraswat model predicts that the retardation of the oxidation rate of nc-Si is caused by the stress induced near Si/oxide interface. The data derived from oxidation process is fit to this model as shown in the solid lines of Figure 3. The oxidation rate is given by

$$\frac{dx}{dt} = \frac{1}{N} \frac{C^*}{1/k_2 + (1/h)[a/(a+x)]^2 + (1/D)a\{1-a/(a+x)\}}$$

for nc-Si, and

F5.3.3
\[
\frac{dx}{dt} = \frac{1}{N} \frac{C^*}{1/k_s + 1/h + (1/D)x} \tag{2}
\]

for Si(100). \( N \) is the number of oxidants required to form a cubic unit of oxide, \( k_s \) is the surface reaction rate constant, \( h \) is the surface mass transfer constant of oxidant, \( D \) is the diffusivity of oxidant in the SiO\(_2\) and \( C^* \) is the oxidant solubility in the SiO\(_2\). The dimensions and stresses of the nc-Si dot are illustrated in Figure 4. The relative importance of the diffusivity and surface reaction terms in determining the oxidation rate is illustrated in Figure 5, where the values of \( \{1 - a / (a + x)\} \) versus \( x \) are plotted for different radii of nc-Si. The straight line \( y = x \) representing planar oxidation is superimposed as a reference. The curve for nc-Si indicates that the coefficient of the diffusion term remains small for different oxide thickness, and the surface reaction tends to dominate. Diffusivity used here is not changed by stress. This result is physically reasonable because, when there is an ample supply of oxidants, surface reaction becomes the bottleneck. Therefore, the growth of oxide on nc-Si is mainly controlled by the surface reaction.

There are two types of stress that can retard 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 \( \sigma_n \) generated at Si/oxide interface, as depicted in Figure 4.

\[
P = 4\eta\xi \frac{1}{b^3} \tag{3}
\]

\[
\sigma_n = -4\eta\xi \left( \frac{1}{a^3} - \frac{1}{b^3} \right) \tag{4}
\]

where \( \eta \) is viscosity, \( \xi \) is velocity constant derived from the oxidation rate at interface. In this equation a “+” sign denotes tension, “-” sign compression. The normal stress is low in thin oxide and increases with oxide thickness. In the case of tensile stress this trend is reversed. The values of these stresses versus the oxidation time are plotted in Figure 6. The values used to calculate the curves in Figure 6 are deduced from the fitting of the observed data for nc-Si dots with 20 nm initial diameter and at an oxidation temperature of 850 °C. These things are physically reasonable since the normal stress is low at high oxidation rate, and gradually increases as the
oxidation rate is retarded. In other words, the oxidation rate rapidly increases initially, and then decelerates for long time oxidation.

These stresses affect the reaction rate constant $k_s$, diffusivity $D$ and solubility $C^*$.

\[
k_s = k_0 \exp \left\{ \frac{\sigma \times (\Omega_{SiO_2} - \Omega_{Si})}{kT} \right\}
\]

(5)

\[
D = D_0 \exp \left( \frac{P \times V_a}{kT} \right)
\]

(6)

\[
C^* = \beta \times C^*_0 \exp \left( \frac{P \times V_s}{kT} \right)
\]

(7)

where $\Omega_{SiO_2} = 45 \text{ Å}^3$ is the molecular volume of SiO$_2$, $\Omega_{Si} = 20 \text{ Å}^3$ is the atomic volume of Si, $k_0$ is the stress-free value of $k_s$, $D_0$ is the diffusivity under 1 atm, $V_a$ is the activation volume of diffusivity, $C^*_0$ is the zero pressure solubility, $\beta$ is an empirical parameter and $V_s$ is the activation volume of solubility. The surface reaction rate constant $k_s$ gradually decreases as the normal stress compressively increases, thus the oxidation rate becomes to be retarded. $\beta$, $V_a$, $V_s$ are the fitting parameters. $V_a (= 6.0 \times 10^{-28} [\text{m}^3])$, $V_s (= 1.5 \times 10^{-29} [\text{m}^3])$ are independent on temperature and particle size in this study. The latter is proved by theoretical and empirical knowledge of the pressure effect on solid solubility [7]. The oxidant solubility in the SiO$_2$ is low compared to planer Si even if there is no stress in SiO$_2$.

High-pressure physics [8], [9] predicts that viscosity should have the opposite temperature and pressure dependence. The relationship of viscosity under pressure in Eq. 8 is reported Dane and Birch [10] and applied in this model.

\[
\eta = \eta_0 \exp(-\alpha \times p)
\]

(8)

where $\eta_0$ is the viscosity at zero pressure, and $\alpha$ is an empirical parameter. The viscosity at zero pressure $\eta_0$ is generally estimated as a function of temperature and the value decreases with higher temperature. This observation was obtained by EerNisse [11] from measurements of wafer bending caused by mismatch of temperature coefficients during cooling and by
Hetherington et al. [12] from direct mechanical measurement of bulk silicate glasses. In our investigation, however, opposite trend is observed as shown in table 1. This may be a result of small particle size and is the subject of further study.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Initial diameter of nc-Si [nm]</th>
<th>( \eta_0 ) [poise]</th>
<th>( \alpha ) [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>10</td>
<td>( 8.5 \times 10^{11} )</td>
<td>( 1.0 \times 10^{-12} )</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>( 1.0 \times 10^{11} )</td>
<td>( 1.0 \times 10^{-12} )</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>( 1.1 \times 10^{12} )</td>
<td>( 1.0 \times 10^{-12} )</td>
</tr>
<tr>
<td>850</td>
<td>15</td>
<td>( 6.0 \times 10^{11} )</td>
<td>( 1.5 \times 10^{-8} )</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>( 1.2 \times 10^{12} )</td>
<td>( 1.5 \times 10^{-8} )</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

It was observed that the oxidation rate of nc-Si was significantly retarded as compared to a Si(100) wafer. This phenomenon is attributed primarily to normal stress. The normal stress diminishes the surface reaction rate constant, which decreases the overall oxidation rate of nc-Si because the oxidation rate is mainly dominated by the surface reaction rate constant.

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**REFERENCES**