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SURFACE STRESS IN SILICON OXIDE LAYER

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We present the evolution of surface stress during plasma oxidation of Si(100) at the oxide film thickness from 0 to 5 nm. We measured surface stress evolution during oxidation with applying positive bias to the samples and observed 5 stages in surface stress. The stress curve depending on oxidation time showed a quick build-up of compressive stress, it's followed by a tensile stress formation, gradually changed to tensile one and compressive stress appeared again. Next, the stress changed very slowly to tensile stress with further oxidation , and finally, compressive stress appeared and it did not changed to tensile one. For the cases of oxidation with applying negative biases, stress curves showed different time dependence from that with positive bias.

Key words : surface stress, silicon oxide layer, plasma oxidation

1. INTRODUCTION

Oxidation of silicon is the most important process in modern semiconductor technology and there are several techniques to make silicon oxide films such as thermal oxidation and plasma oxidation. The thermal stresses in the oxides occuring at the high-temperature processing casue a degradation of reliability of the metal-oxide-semiconductor (MOS)-devices. The intrinsic stress due to lattice mismatch at the interface of silicon and silicon oxide has to be considered, in additon. There are several papers on the experimental study on the stresses induced by oxidation of silicon. Kobeda at al. have measured the intrinsic stress in silicon oxide films of 10 to 1000 nm thickness, and observed a compressive stress due to the lattice mismatch1).The surface stresses of silicon induced by adsorption of oxygen gas have been reported by Sander and Ibach2). They reported that adsorbate-induced surface stress occuring within monolayer oxygen coverage depends on the surface orientation. However, there is no report on the suraface stress during growth of oxide films of a few nanometers thickness which is requred as gate insulators in next generation MOS-devices. We present evolution of surface stress during the ultrathin oxide growth (0-5 nm) by a plasma oxidation of Si(100). Detailed sample-bias dependence of the surface stress evolution is discusssed.

2. EXPERIMENTAL

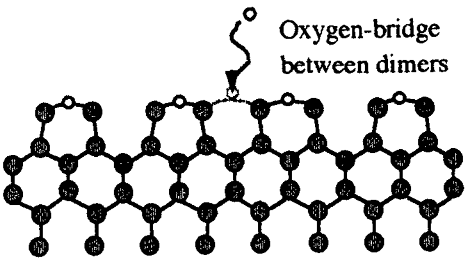
The oxidation experiments were performed at room temperature in a UHV system. The base pressure was less than 1 x 10^{-7} Pa with an ion pump and a turbo molecular pump. The sample was a beam of a Si(100) microcantilever with dimensions 450 x 50 x 4 μm. Before the oxidation, the cantilever was pre-treated by immersing in HF solution, rinsing in water, and annealing at 700 °C in the UHV chamber. The plasma was generated by an RF discharge of oxygen gas at 13.56MHz with a power of 500 W. Oxygen gas pressure was 1.3 x 10^{-1} Pa. The applied dc bias to the samples was varied from -60V to +60 V. Langmuir probe measurements showed that the oxygen plasma density was 10^8/cm^3, and the plasma potential was +15V near the sample.

Oxidation of a front side of the cantilever causes bending of the lever due to the stress formation, and the deflection of the free end was detected from the change in the reflection angle of laser beam from the lever back side. Stress (σ) was calculated from the lever deflection(δ) using Stony's formula3),

$$\sigma = \delta E h^2 / 3L^2(1-v)t .$$

Here L and h are the length and the thickness of a cantilever, E is Young's modules, v is the Poisson ratio of a lever and t is the thickness of oxide layer. It is in general hard to determine thickness of ultra thin films in a nanometer scale. Thus, in this work, the surface stresses are expressed as $t\sigma$ [N/m]. The sensitivity in the deflection was less than 0.1 nm which corresponds to total stress 2 x 10^{-4} N/m. The temperature of the samples is expected to rise by exposing them to the plasma. We evaluated the temperature rise by means of the bimetallic effect using an Al-

(a) O into (2x1) dimer



(b) top surface shrinkage

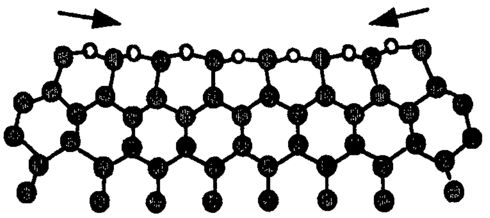


Fig.3 A model of shrinkage of Si (100) top surface oxidation. (a) Side view of (2 X 1) dimer structure. Adsorption of oxygen in each dimer bond. The distance of dimer and dimer becomes short. (b) Adsorption of oxygen between dimer and dimer. The oxygen bridge makes the surface shrinkage.

The reason of the formation of tensile stress in the stage (IV) is not clear at present. One of the possible explanations is phase transformation of the oxide layers from crystal to amorphous. The compressive stress observed in last stage (V) can be qualitatively explained in terms of the lattice misfit between the Si substrate and the oxide layer. However the lattice parameter of silicon oxide is 30 % lager than that of silicon as the substrate, and the compressive stress estimated from the misfit model is much less than the observed. Studies on the structures of the silicon/oxide interface is of importance for further understanding.

3.2 The stress changes under negative biases.

For negative biases, the surface stresses showed different time dependence from those for the positive biases. Fig. 2 (b) shows surface stress at a sample bias of -60V. There occur only three stages. We do not see the first two stages which were observed in the case of positive biases. The oxidation induces a quick build-up of compressive stress, instead. For the long time oxidation, there was no distinct difference in the surface stress evolution from those for the negative biases.

In the case of positive biases we explained the first compressive stress in terms of the excess electron charge effects. This dose not occur in the case of negative biases, because the first stage (I) inflowing of electrons to the samples are disturbed by retarding field of the biases. On the other hand, many of positive ions of O^+ and O^{2+} under the biases would go into deeper layer of the silicon substrate, just passing through the surface region under the bias, since they have rather higher kinetic energies accelerated by the biases[9)]. Say in other words, the oxidation of the top surface is not important, but deeper layers are oxidized even from very initial stage of oxidation. This could explain the absence of the tensile stress formation (II) which was seen for the positive biases and the appearance of the compressive one instead. Except the very initial stage the stress changes were very similar to those for the positive biases; the stress changed to tensile and finally became compressive. The origins of the stresses under the positive and negative biases are suggested to be similar.

4. CONCLUSION

We have measured evolution of surface stress of Si(100) during plasma oxidation with applying positive and negative sample biases at film thickness from 0 nm to about 5 nm, and found five stages in stress curve with positive bias and three stages in that with negative bias. It is known only the compressive stress observed and which is explained in term of lattice misfit. But in the paper we report compressive and tensile stresses appeared over again with a oxide layer growth in a condition of positive bias applying. Some of these stresses are depend on the surface structure of surface as dimer. The difference in stress curve of positive bias and negative bias at initial part oxidation could be explain with differ of plasma elements and their kinetic energies.

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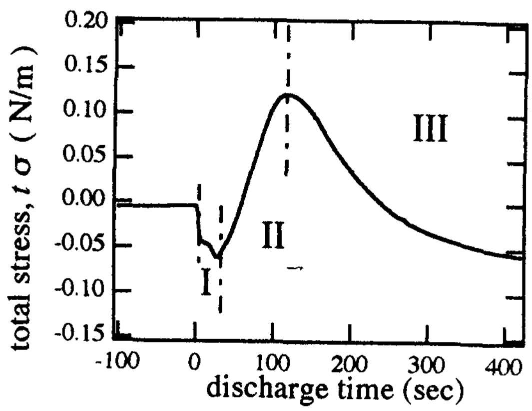
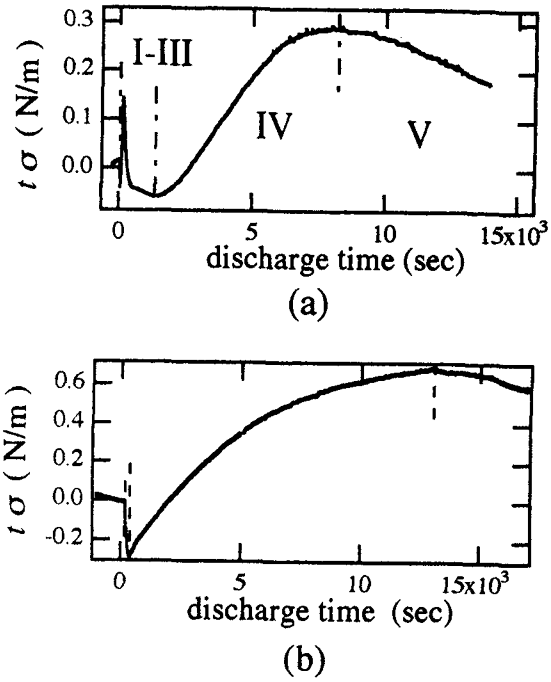


Fig.1 The change in surface stress during plasma oxidation at initial oxidation. Oxidation was made by rf discharge O_2 plasma with 13.5MHz, 500W. The Si(100) sample was applied bias +45V during operation. Total stress, *ts* >0 corresponds to tensile stress and *ts* < 0 corresponds to compressive stress.



(a)

(b)

Fig.2 The change in surface stress during plasma oxidation. (a) Sample was applied bias +45Vduring oxidation. (b) Applied bias -60V.

coated cantilever. The temperature increased 1 degree at maximum for 4 hours oxidation. This was estimated to cause a deflection of only 0.08 nm and is negligible for the stress measurements.

From real time ellipsometry measurements, we know that the growth kinetics of the plasma oxidation is strongly dependent on the sample bias[4]. Using the refractive index of bulk SiO_2, the oxide film thickness was estimated to be roughly 5 nm at a bias of +45V and 2.5 nm at -60V, for the 10000 sec oxidation. The film growth was very gentle and AFM observation showed that the top surface was so smooth, suggesting the layer by layer oxidation[5]. After the oxidation experiments the AES measurements showed that oxidation of back side of the cantilever was negligibly low compared with that of the front.

3. RESULTS AND DISCUSSION

3.1. The stress changes under positive biases.

Figure 1 shows a surface stress change for a 45V bias in the first several minutes. The oxidation first induces a quick build-up of compressive stress (I), followed by a tensile stress formation (II). Then, the stress changes to be compressive (III). For further oxidation, the stress gradually becomes tensile again (IV) and finally compressive (Fig. 2(a)). Essentially the same behaviors were observed for other positive biases.

The quick build-up of compressive stress in the first stage(I), which was not observed for a non-biasing oxidation[6], is not due to oxidation of silicon surface. This stress change occurred not only on clean Si surfaces, but also on oxidized surfaces when re-switching on the plasma, suggesting that the initial compressive stress should be caused by an instability of the plasma on the ignition. It is known that collision of electrons to the surfaces promotes the oxidation[4]. We measured the electron currents during the plasma oxidation, and observed an extraordinarily-large increase in the electron current upon the plasma ignition. The excess charge could weaken Si-Si bonds which results in the increase of bond length, inducing the initial compressive stress.

A recent theoretical calculation based on a periodic slab model suggests the importance of surface dimers for the surface shrinkage. In the model, the oxygen-bridged dimer structure perpendicular to the dimer rows is responsible for a tensile stress on the Si(100) surfaces[7] (see Fig.3). The Si(100) surface consists of domains of (2 x 1) and (1 x 2)[8]. The two domains are next to each other, and covers roughly equal areas after the annealing. The cantilever used here has a length side parallel to the <011>-axis. We think that dimer rows perpendicular to the length side of the cantilever should contribute to the tensile stress but those along the length side not.

The compressive stress in the third stage (III) is on account of the attacks of oxygen atoms to Si-Si back bonds in deeper layers. The insertion of O expands Si-Si bond resulting in the compressive stress macroscopically.

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