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Planarized Deposition of High Quality Silicon Dioxide Film by Photo-Assisted Plasma CVD at 300°C Using TEOS

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High quality silicon dioxide films were deposited by a photo-assisted plasma CVD (PAP-CVD) method using tetraethyl orthosilicate (TEOS) and oxygen at 300°C. Oxygen gas was excited in a high density plasma which was kept apart from a substrate. Excited oxygen was effectively transported to a deposition chamber and reacted with TEOS gas to generate reactive intermediates. The adsorbed intermediates migrated sufficiently for conformal coverage on the substrate surface and were photo-excited to produce high quality silicon dioxide films. Aluminum lines with 0.7 μm step was able to be successfully planarized with the high quality silicon dioxide film. The planarization mechanism was discussed using a site-by-site migration model.

1. INTRODUCTION

A new planarization method of depositing dielectric interlayer is required in submicron VLSI process. Spin-on-glass (SOG) formed between two SiO_2 layers by atmospheric pressure CVD (AP-CVD) method is widely used because of its planarization capability. However, cracks sometimes occur in the SOG film and complicate processes are required. SiO_2 films by plasma enhanced CVD (PE-CVD) method using alcohoxysilane, such as tetraethyl orthosilicate (TEOS), is not sufficient for practical use, because the step coverage is not conformal and carbon atoms are easily incorporated in the film.(1) Although, SiO_2 films by AP-CVD method using TEOS and O_3 have conformal step coverage, the film quality is poor when depositing below 400°C.(2)

The poor step coverage in the PE-CVD method is considered to be caused by the inadequate reaction in a vapor phase to prevent the surface migration. The carbon incorporation in the PE-CVD method is considered to be caused by the inadequate reaction on the substrate surface, such as the C-H bond dissociation by incident ions. We have reported the photo-assisted plasma CVD (PAP-CVD) method for the deposition of high quality SiN films.(3) In the PAP-CVD method, N_2 gas is excited through plasma which is kept apart from a substrate and the surface reaction is induced by light irradiation.

In this paper, we report the deposition of SiO_2 films with conformal step coverage, low stress and high quality by the PAP-CVD method at low temperature.

2. EXPERIMENTAL

Figure 1 shows a schematic of the PAP-CVD apparatus. The rf plasma was generated in a quartz tube (33 mmØ and 210 mm length) with capacitance coupled electrodes. The typical rf power was 200 W. The high density plasma with an plasma density of $2X10^{10}$ cm^{-3} was confined in the quartz tube. The plasma density near the substrate was as low as $2X10^{8}$ cm^{-3} at the pressure of 0.1 Torr. The sheath potential between the plasma and the substrate was as low as 30 V. The Xe illuminator, whose emission peak was at 400 nm, was used as a light source, because the absorption of the adsorbed intermediates was at near ultra-violet region. The illumination intensity on the substrate was

$0.6\ W/cm^2$. The number of effective photon was much larger than that of adsorbed intermediates. By the irradiation, the substrate surface was heated up to 300°C. O_2 gas was introduced through the plasma and TEOS was introduced near the substrate. The typical operating pressure was 0.1 Torr. The typical flow rate of O_2 and TEOS were 200 and 10 sccm, respectively. SiH_4 gas was used for comparing with TEOS under the same condition.

3. RESULTS AND DISCUSSIONS

Figure 2 shows the IR absorption spectra of the deposited films (a) without the irradiation and without the resistive heating using TEOS, (b) without the irradiation and with the resistive heating using TEOS, (c) with the irradiation using TEOS and (d) with the irradiation using SiH_4. In the all cases, the O_2 gas was excited by the rf plasma in the quartz tube. O-H, C=O, Si-O-C and Si-O-H vibrational bands were observed in (a) of Fig. 2, since the intermediates generated by the incomplete vapor phase reaction was directly deposited on the substrate. O-H, Si-O-H and Si-O-C weak bands still remained in (b) of Fig. 2, because the ethyl groups in the adsorbed intermediates were not sufficiently extracted by the resistive heating. Only Si-O bands were observed in (c) of Fig. 2. The photochemical surface reaction was confirmed to be effective to extract the ethyl groups from the adsorbed intermediates. The film purity by the PAP-CVD method using TEOS was as high as that using SiH_4 of (d) in Fig. 2. The etching rate of the PAP-CVD SiO_2 film by BHF was 2.6 times larger than that of thermally oxidized SiO_2, and was much smaller than that of the low-temperature CVD SiO_2 films using TEOS. The tensile stress was as low as $3X10^8$ dyn/cm^2 and the cracks were not observed.

Figure 3 shows the SEM photographs of cross-sectional view of the films on Al lines on Si substrate. The step height was 0.7 μm. When the thickness of SiO_2 films was equal to that of Al steps, a conformal step coverage was achieved as shown in (a) of Fig. 3. The coverage became to the planar shape with the increase of the film thickness as shown in (b) of Fig. 3. The Al lines were successfully planarized with the high quality

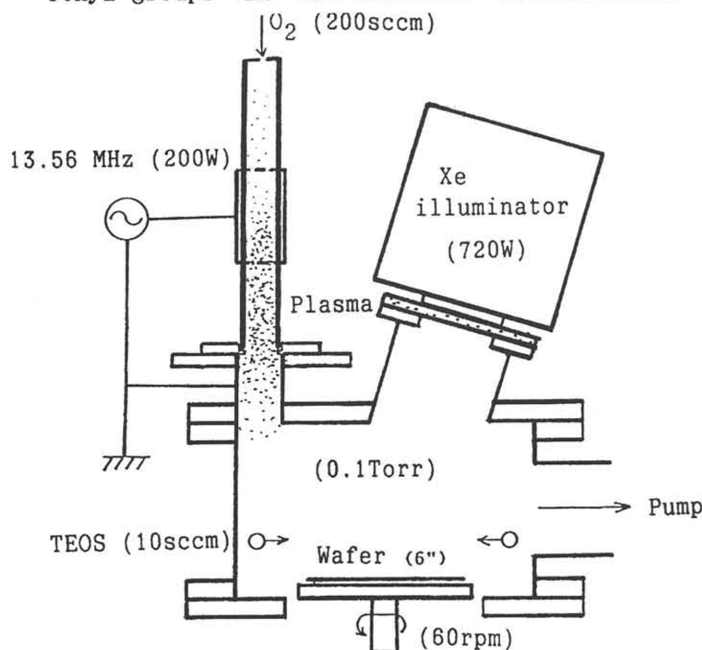

Fig. 1. Schematic of PAP-CVD apparatus.

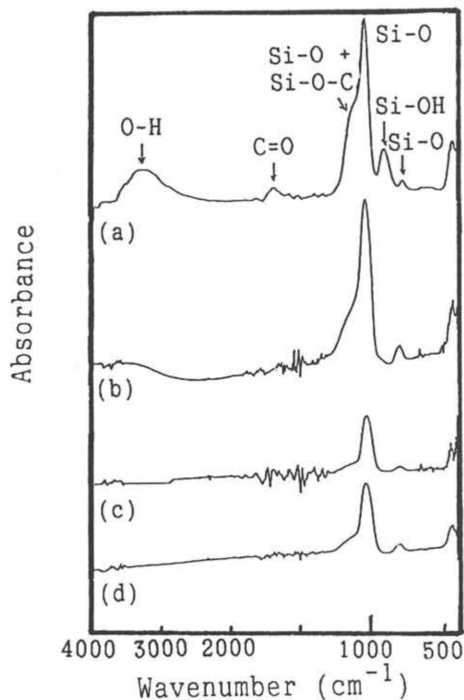

Fig. 2. IR spectra (a) without irradiation and without heating using TEOS, (b) without irradiation and with heating using TEOS, (c) with irradiation using TEOS and (d) with irradiation using SiH_4.

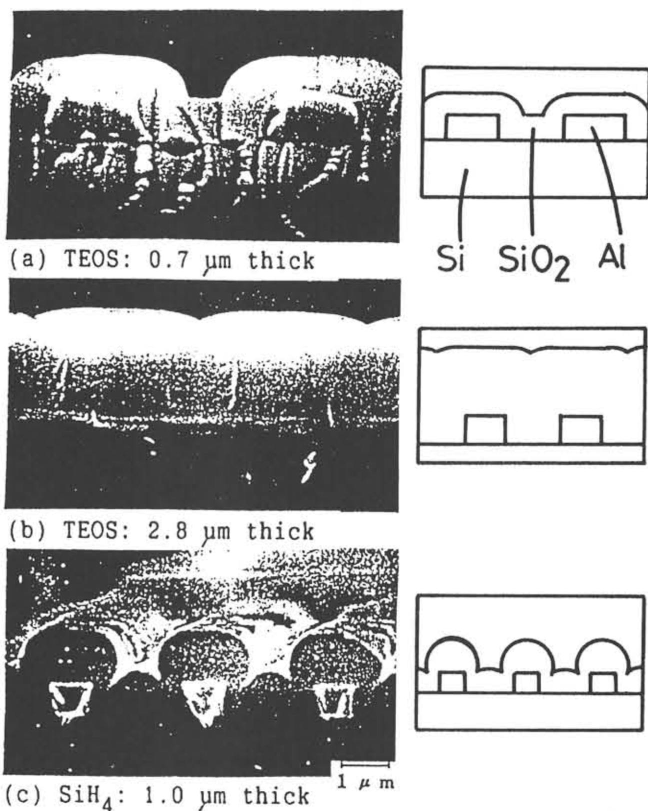

Fig. 3. Step coverage.

SiO_2 film by the PAP-CVD method using TEOS and O_2. Although high quality SiO_2 films were deposited by the PAP-CVD method using SiH_4, the step coverage was mouse-ear like as shown in (c) of Fig. 3. The mouse-ear like coverage is not adequate for the dielectric interlayer in submicron VLSI.

To explain the difference of the step coverage when comparing the source gases or comparing the deposition methods, the mean migration length was estimated using a site-by-site migration model. Figure 4 shows a schematic of the site-by-site migration model. The adsorbed intermediates migrate to the neighbor adsorption sites toward random direction interacting with the substrate surface.

The migration frequency N of the adsorbed intermediates to the neighbor adsorption sites during time t is

$$N=Z\nu_0 t\cdot\exp(-\overline{Em}/kT) \quad (1),$$

where Z is the number of the neighbor adsorption sites, ν_0 is the libration

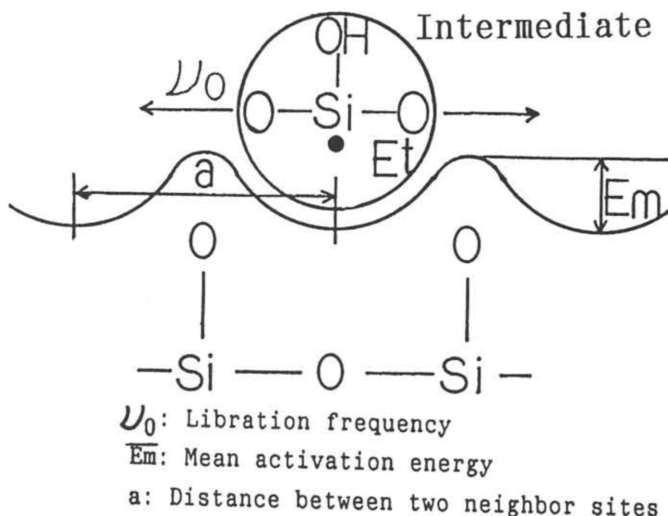

Fig. 4. Schematic of site-by-site migration model.

frequency along the surface, and $\overline{Em}$ is the mean activation energy for migration. The existance probability of the intermediates in the distance Lm to Lm+dLm from the first adsorbed site after the N-times site-by-site migrations toward random direction, P(Lm), is statistically obtained as

$$P(Lm)dLm=dLm/(2\pi N)^{1/2}a(1-(Lm/Na)^2)^{1/2}$$
$$(1-(Lm/Na)^2)^{N/2}(1+Lm/Na)^{Lm/2a}$$
$$(1-Lm/Na)^{-Lm/2a} \quad (2),$$

where a is the distance between two neighbor sites. The mean migration length $\overline{Lm}$ is given by

$$P(\overline{Lm})dLm/P(0)dLm=1/e \quad (3).$$

By inserting Eq. (2) to Eq. (3),

$$(1-(\overline{Lm}/Na)^2)^{1/2}(1-(\overline{Lm}/Na)^2)^{N/2}$$
$$(1+\overline{Lm}/Na)^{\overline{Lm}/2a}(1-\overline{Lm}/Na)^{-\overline{Lm}/2a}=e \quad (4).$$

When N is much larger than unity, $\overline{Lm}$/Na becomes zero. The mean migration length $\overline{Lm}$ can be given by the limit of the logarithm of Eq. (4) as $\overline{Lm}$/Na approches to zero. The mean migration length $\overline{Lm}$ is

$$\overline{Lm}=(2N)^{1/2}a \quad (5),$$

and

$$\overline{Lm}=(2Z\nu_0 t\cdot\exp(-Em/kT))^{1/2}a \quad (6)$$

by inserting Eq.(1) to Eq.(5).

Figure 5 shows the calculated mean migration length $\overline{Lm}$ as a function of the mean activation energy for migration $\overline{Em}$ using Eq. (6). Z, ν_0, t, T and a were supposed to be 3, $1X10^{12}$ sec^{-1}, 1 sec, 573 K, and 3.6 Å, respectively. The $\overline{Lm}$ depended strongly on the $\overline{Em}$ as shown in Fig. 5. In order to obtain a conformal step coverage as shown in Fig. 4, the mean migration length $\overline{Lm}$ should be larger than the value of the Al step height. When the Al step height is 0.7 µm as shown in Fig. 3, the activation energy for migration $\overline{Em}$ should be less than 0.7 eV. In the CVD method using SiH_4 or in the PE-CVD method even using TEOS, the adsorbed intermediates were considered to include many non-pair electronic states, namely radical states. In these cases, since the covalant bonds are easily formed between the intermediates and the substrate surface at the first stage of migration, the activation energy for migration $\overline{Em}$ is large as shown in Fig. 5. Hence, the step coverage was not conformal in the case of the CVD method using SiH_4 as shown in

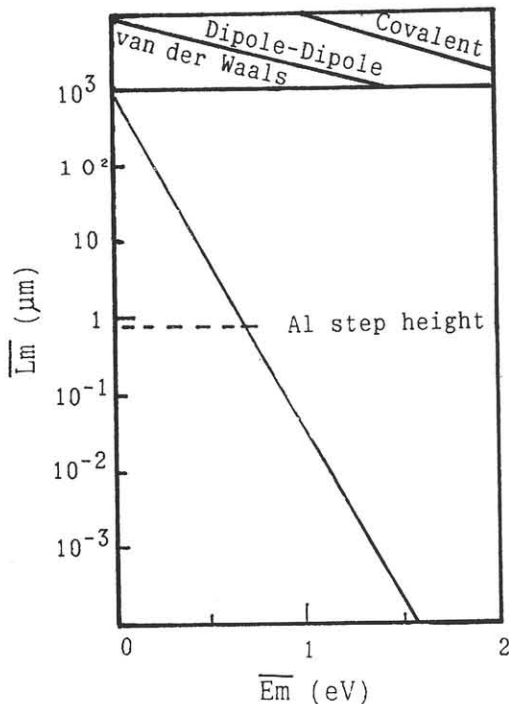

Fig. 5. Calculated mean migration length $\overline{Lm}$ vs. mean activation energy $\overline{Em}$ using eq. (6).

(c) of Fig. 3. On the other hand, in the PAP-CVD method using TEOS, since the plasma vapor reaction was suppressed, the intermediates were able to be adsorbed on the substrate surface with the weak interaction, such as van der Waals force, i.e., the $\overline{Em}$ is small as shown in Fig. 5. The step coverage was, therefore, conformal in the PAP-CVD method using TEOS as shown in (a) of Fig. 3. In spite of the incomplete vapor reaction, high purity SiO_2 film was deposited by PAP-CVD method. Since the plasma was generated apart from the substrate, the inadequate reaction, such as C-H bond dissociation by incident ions, was considered to be suppressed. Furthermore, the volatile components, which included ethyl group, were easily extracted from the adsorbed intermediates by the irradiation. Consequently the high purity SiO_2 film with conformal step coverage was able to be deposited by the PAP-CVD method using TEOS.

4. CONCLUSIONS

Silicon dioxide films with conformal step coverage, low stress and high quality were deposited at low temperature by photo-assisted plasma CVD method using TEOS and O_2. The silicon dioxide film fabricated by PAP-CVD method has the potential for being used as the dielectric interlayer in submicron VLSI.

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