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## Silicon dioxide deposition at 100 °C using vacuum ultraviolet light

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A new photochemical reaction for low-temperature deposition of silicon dioxide has been developed. In this process silane is reacted with nitrogen dioxide in the presence of vacuum ultraviolet radiation. The electrical and mechanical properties of films grown at 100 °C are reported. Capacitance voltage measurements on metal-oxide-semiconductor structures on silicon indicate an interface state density  $< 5 \times 10^{11}/\text{cm}^2$ . Several possible reaction mechanisms are discussed, and evidence is presented indicating surface photochemistry may be important.

Thin films of silicon dioxide are used extensively as insulators in the fabrication of many semiconductor devices. Silicon dioxide films deposited by chemical vapor deposition typically require temperatures near 800 °C. However, some processes, such as the fabrication of devices with multilevel aluminum interconnects, require deposition temperatures below 350 °C. Several techniques have been developed for low-temperature deposition of silicon dioxide including plasma assisted deposition,<sup>1</sup> low-pressure chemical vapor deposition,<sup>2</sup> and photoassisted chemical vapor deposition. Some photochemical deposition reactions<sup>3</sup> use Hg vapor as a photochemical catalyst to decompose nitrous oxide in the presence of silane. Films deposited with these reactions have been found to have adhesion problems, and tend to be incompletely oxidized. Several other deposition reactions using photodissociation of molecular oxygen<sup>4</sup> or disilane<sup>5</sup> have been reported. In this letter we report a new reaction in which vacuum ultraviolet (VUV) light (1066 Å) is used to initiate a reaction between nitrogen dioxide and silane thus forming silicon dioxide.

Vacuum ultraviolet irradiation has two advantages over other light sources. First, it aides in fully oxidizing the silicon dioxide. It has been shown that exposure of incompletely oxidized silicon dioxide to ultraviolet radiation causes the silicon dioxide to become completely oxidized.<sup>6</sup> Second, exposure of the substrate to VUV irradiation, prior to the deposition, removes some contaminants from the surface.<sup>7</sup>

The use of nitrogen dioxide has an important advantage over photoreactions where nitrous oxide is used. Nitrogen dioxide is a strong oxidant and by having a large excess present any reduction of native oxides by the silane can be prevented. In experiments using this reaction to passivate InSb and HgCdTe, the native oxide was preserved during film deposition.<sup>8</sup>

The deposition reactions were performed in a low-pressure reactor with a windowless, microwave excited, argon discharge lamp (1066 Å) used for a light source. The photon flux was determined by measuring the photoelectron yield from a gold substrate. The flux was determined to be  $3 \times 10^{14}$ photons/cm<sup>2</sup> s at a distance of 4 cm from the end of the lamp (this is a lower bound, the flux could be as much as a factor of 3 higher). The argon flow was adjusted to maintain the partial pressure of argon at 3 Torr inside the chamber. The silane and nitrogen dioxide are mixed before entering the reactor chamber, and the flow of each gas is regulated by mass flow controllers. The flow rate of NO<sub>2</sub> and SiH<sub>4</sub> was 40 and 3 sccm, respectively. The pumping speed was adjusted to maintain a partial pressure of 0.25 Torr of  $NO_2$  inside the chamber. The substrate was placed on a heated stage 4 cm from the end of the lamp, and the temperature was set between 25 and 250 °C. The substrate was exposed to VUV radiation for 10 min prior to the growth of SiO<sub>2</sub>.

Physical properties of the films are consistent with those of higher temperature thermally deposited silicon dioxide. Oxides grown on silicon at 250 °C had an etch rate of 2500 Å/min in BOE 930. This is comparable to oxides grown at temperatures of 600 °C by thermal chemical vapor deposition. The step coverage of the films was examined by depositing 2000 Å of SiO<sub>2</sub> on 1  $\mu$ m mesas, a scanning electron micrograph is shown in Fig. 1. The index of refraction of the silicon dioxide was between 1.45 and 1.47, indicating that the film is fully oxidized. Infrared spectra were taken in the reflection mode on a Nicolet MX-1 FT spectrometer. A spectrum of SiO<sub>2</sub> on Si grown at 110 °C is shown in Fig. 2. The lack of any band at 2300 cm<sup>-1</sup> indicates there is not much hydrogen in the form SiH present in the SiO<sub>2</sub>. The detection limit of SiH by infrared spectroscopy is about 1%. The SiO stretch is at 1073 cm<sup>-1</sup> consistent with previous measurements9 of the SiO stretch for fully oxidized silicon dioxide.

The stoichiometry of the films was found to be largely independent of the ratio of  $NO_2$  to  $SiH_4$  giving fully oxidized  $SiO_2$ . If the partial pressure of  $NO_2$  was too high, less dense



FIG. 1. Scanning electron micrograph of 2000 Å film grown at 110 °C on 1  $\mu$ m silicon mesas.

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FIG. 2. Reflection infrared spectrum of 3000 Å of silicon dioxide on silicon grown at 110 °C.

films were observed, presumably due to an increase in gas phase nucleation giving large  $SiO_2$  grains. At partial pressures of NO<sub>2</sub> above 0.35 Torr very little  $SiO_2$  growth was observed.

Metal-oxide-semiconductor structures were made with silicon dioxide on n- and p-type silicon. A capacitance versus voltage (C-V) curve for one of these samples grown at 110 °C is shown in Fig. 3. Analysis of C-V data indicates that the trapped charge density ranges between 10<sup>9</sup> and 10<sup>11</sup> per cm<sup>2</sup>, depending on growth conditions, with the sign of the fixed charge being negative in most cases. It was found that increasing the ratio of SiH4 to NO2 decreased the amount of negative fixed charge in the films. Films grown at higher temperatures also have lower amounts of fixed negative charge. Both of these observations are consistent with the negative charge being due to nitrogen dioxide trapped in the film. The interface state density was determined by taking the difference between the quasistatic and 1 MHz C-V curves  $(N_{ss} = 5 \times 10^{10} - 5 \times 10^{11} \text{ per cm}^2)$ . Low leakage currents were measured for 600-Å-thick films; the leakage current was 5  $\mu$ A at 5 V, 10  $\mu$ A at 24 V, and 15  $\mu$ A at 52 V. Bias temperature stress measurements were made by applying a 5-V bias and raising the temperature to 250 °C. These resulted in a positive 2.5-V shift in the flatband voltage, indicating a large number of electron traps at the interface. These electron traps may be due to nitrogen dioxide in the films and we are investigating how to reduce this shift.

It is observed that the initial growth rate is highly dependent upon the substrate material. The growth rate was typically around 100 Å per min on silicon. However, the initial growth on HgCdTe is observed to be 30% faster than the growth on silicon, which in turn is 20% faster than the growth on gallium arsenide. The growth of silicon dioxide is found to be limited to the area being illuminated by the lamp, and the thickness falls off rapidly as a function of distance from the center of the lamp. A thin, less dense film is observed to grow on the outer edges of the substrate and on the chamber walls. The dependence of the growth rate upon the light intensity indicates that the primary reaction is photoinitiated and not caused by the discharge.

There are several reactions that occur in the growth of these silicon dioxide films. Silane is photodissociated at wavelengths below 1700 Å with a maximum in the cross



FIG. 3. Capacitance vs voltage curve for 200 Å of silicon dioxide grown at 110 °C on *n*-type silicon.

section at 1150 Å.<sup>10</sup> This gives silane radicals which can then react with the NO<sub>2</sub> giving SiO<sub>2</sub> [reaction (1)]. Because of the large uncertainty in the photon flux, the quantum yield of the reaction could not be determined.

$$SiH_4 + hv \rightarrow SiH_3 + H$$
  

$$SiH_3 + SiH_3 \rightarrow SiH_2 + SiH_4$$

$$SiH_2 + 3NO_2 \rightarrow SiO_2 + H_2O + 3NO.$$
(1)

NO<sub>2</sub> will also photodissociate at these wavelengths giving atomic (<sup>1</sup>D) and molecular oxygen.<sup>11</sup> This oxygen can then react with the silane to form SiO<sub>2</sub>, or it can react with NO<sub>2</sub> to form O<sub>2</sub> and NO. This second reaction is very rapid  $(k = 1 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ .<sup>12</sup> Since there is a large excess of NO<sub>2</sub>, any oxygen atoms generated from its photodissociation will probably react to form O<sub>2</sub> and NO before they can react with silane.

A possible explanation for the substrate-dependent growth rate could be a photoassisted surface reaction. It has been observed that illumination of the surface enhances the thermal oxidation of silicon.<sup>13</sup> One mechanism for the photoassisted surface reaction would be if the irradiation is generating a more reactive surface. The 12-eV photons of the argon discharge lamp are of high enough energy to break silicon oxygen bonds, thus continuously generating reactive surface sites. The observed trend in growth rates correlates well with the dissociation energies<sup>14</sup> of HgO, SiO<sub>2</sub>, and Ga<sub>2</sub>O<sub>3</sub>, the growth rate being slowest on the substrate with the highest native oxide dissociation energy.

In summary, we have demonstrated a new reaction using VUV radiation for depositing silicon dioxide at low temperatures. The reaction produces high-quality fully oxidized silicon dioxide with good electrical and mechanical properties. It is observed that the growth rate is highly dependent upon the substrate material indicating a photosurface reaction could be important in the growth process.

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