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Silicon Dioxide Deposition at 100°C Using Vacuum Ultraviolet Light

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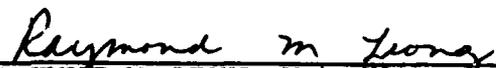
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<p>A new photochemical reaction for low-temperature deposition of silicon dioxide has been developed. In this process silane is reacted with nitrogen dioxide in the presence of vacuum ultraviolet radiation. The electrical and mechanical properties 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.</p>				
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PREFACE

The authors would like to thank Gloria Tao and Robert Egler for their assistance in obtaining infrared spectra and C-V data.

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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 that have been developed for low-temperature deposition of silicon dioxide include plasma-assisted deposition,¹ low-pressure chemical vapor deposition,² and photo-assisted chemical vapor deposition. Some photochemical deposition reactions³ 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 oxygen⁴ or disilane⁵ have been reported. In this document 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 aids 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.⁶ Second, exposure of the substrate to VUV irradiation, prior to the deposition, removes some contaminants from the surface.⁷

The use of nitrogen dioxide has an important advantage over photo-reactions 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.

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 photo-electron yield from a gold substrate. The flux was determined to be

3×10^{14} photons/cm²s at a distance of 4 cm from the end of the lamp (this 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 were mixed before entering the reactor chamber, and the flow of each gas regulated by mass flow controllers. The flow rate of NO₂ and SiH₄ was 40 and 3 sccm, respectively. The pumping speed was adjusted to maintain a partial pressure of 0.25 Torr of NO₂ 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 SiO₂.

Physical properties of the film were 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 deposition 2000 Å of SiO₂ on 1 μm mesas, a scanning electron micrograph of which is shown in Fig. 1. The index of refraction of the silicon dioxide was between 1.45 and 1.47, indicating that the film was fully oxidized. Infrared spectra were taken in the reflection mode on a Nicolet MX-1 FT spectrometer. A spectrum of SiO₂ on Si grown at 110°C is shown in Fig. 2. The lack of any band at 2300 cm⁻¹ indicates there is not much hydrogen in the form SiH present in the SiO₂. The detection limit of SiH by infrared spectroscopy is about 1%. The SiO stretch is at 1073 cm⁻¹, consistent with previous measurements⁸ of the SiO stretch for fully oxidized silicon dioxide.

The stoichiometry of the films was found to be largely independent of the ratio of NO₂ to SiH₄ giving fully oxidized SiO₂. If the partial pressure of NO₂ was too high, less dense films were observed, presumably due to an increase in gas phase nucleation giving large SiO₂ grains. At partial pressures of NO₂ above 0.35 Torr, very little SiO₂ growth was observed.

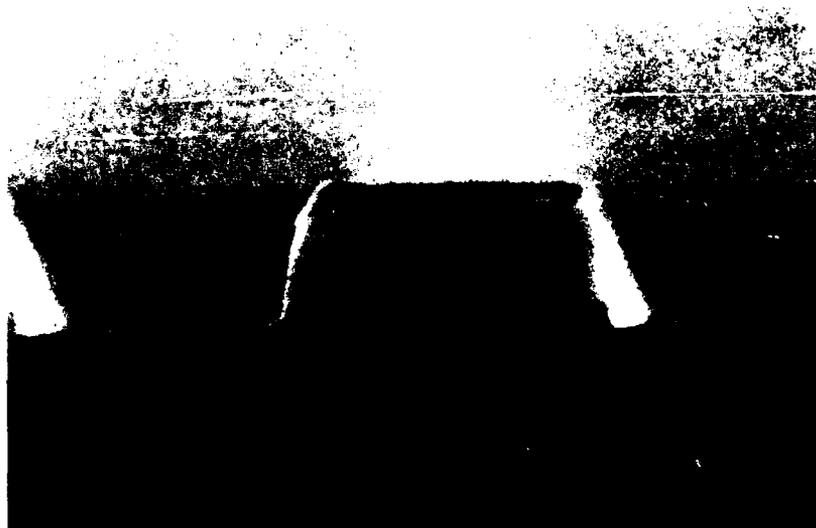


Fig. 1. Scanning Electron Micrograph of 2000 Å Film Grown at 110°C on 1 μm Silicon Mesas

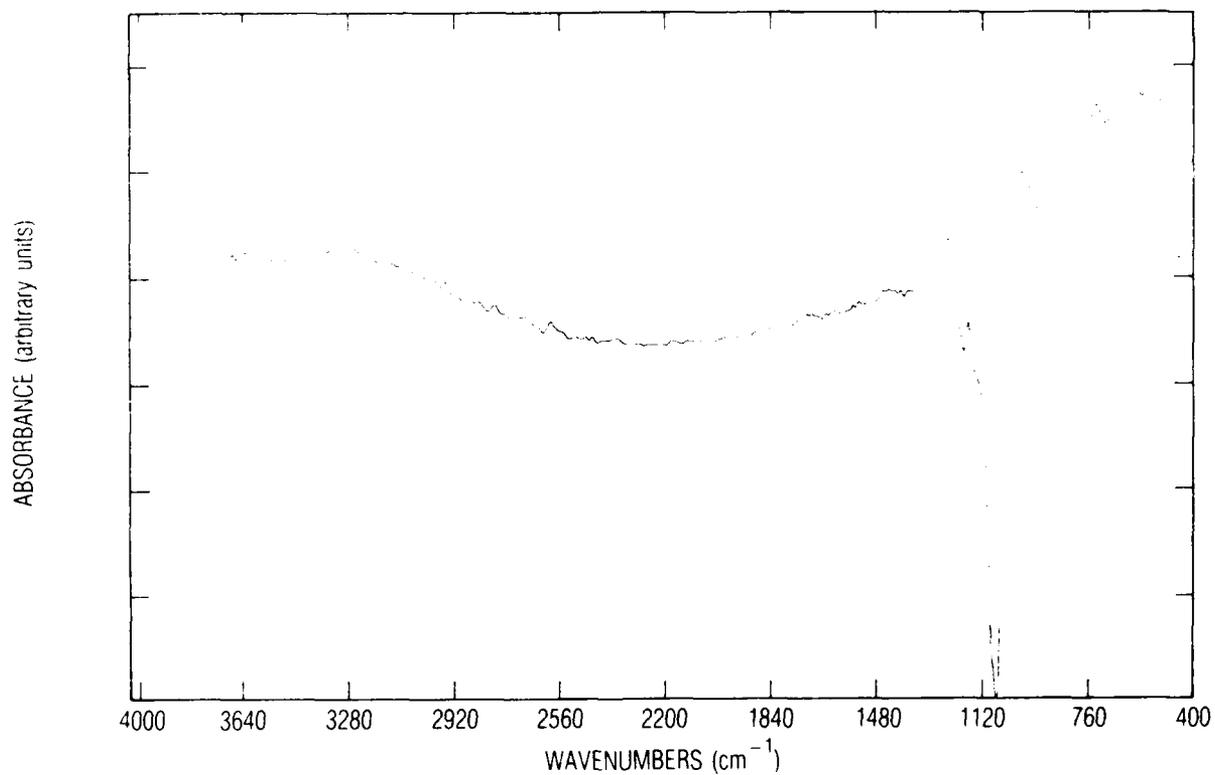


Fig. 2. Reflection Infrared Spectrum of 3000 Å of Dioxide on Silicon Grown at 110°C

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 10^9 and 10^{11} per cm^2 , depending on growth conditions, with the sign of the fixed charge being negative in most cases. It was found that increasing the ratio of SiH_4 to NO_2 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 quasi-static and 1 MHz C-V curves ($N_{\text{SS}} = 5 \times 10^{10}$ - 5×10^{11} per cm^2). Low leakage currents were measured for 600 Å -thick films; the leakage current was 5 μA at 5 V, 10 μA at 24 V, and 15 μA at 52 V. Bias temperature stress measurements were made by applying a 5 V bias and raising the temperature

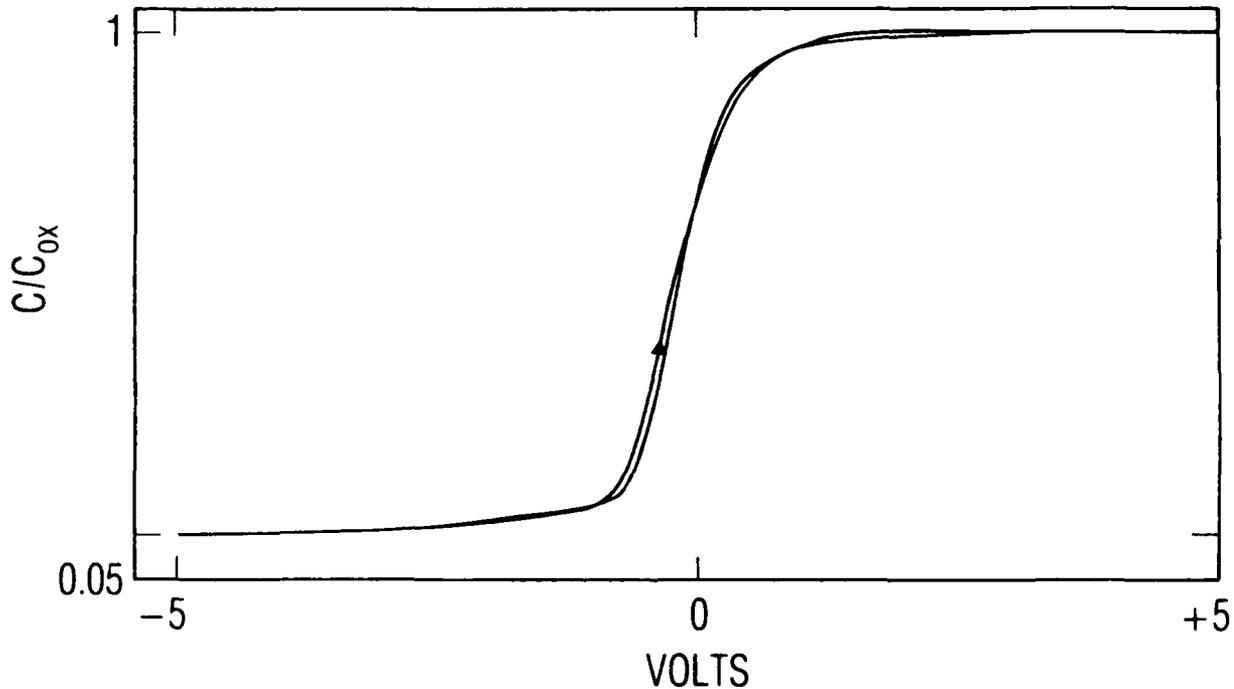
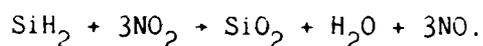
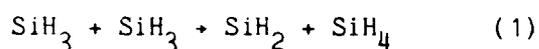
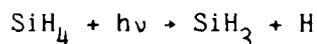


Fig. 3. Capacitance vs Voltage Curve for 200 Å of Silicon Dioxide Grown at 110°C on n-Type Silicon

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 was observed that the initial growth rate was highly dependent upon the substrate material. The growth rate was typically around 100 Å per min on silicon. However, the initial growth on HgCdTe was observed to be 30% faster than the growth on silicon, which in turn was 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 fell off rapidly as a function of distance from the center of the lamp. A thin, less dense film was 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 photo-initiated 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 section at 1150 Å.⁹ This gives silane radicals which can then react with the NO₂ giving SiO₂ [reaction (1)]. Because of the large uncertainty in the photon flux, the quantum yield of the reaction could not be determined.



NO₂ will also photodissociate at these wavelengths giving atomic (¹D) and molecular oxygen.¹⁰ This oxygen can then react with the silane to form SiO₂, or it can react with NO₂ to form O₂ and NO. This second reaction is very rapid ($k = 1 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).¹¹ Since there is a large excess

of NO_2 , any oxygen atoms generated from its photodissociation will probably react to form O_2 and NO before they can react with silane.

A possible explanation for the substrate-dependent growth rate could be a photo-assisted surface reaction. It has been observed that illumination of the surface enhances the thermal oxidation of silicon.¹² One mechanism for the photo-assisted 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 of HgO , SiO_2 , and Ga_2O_3 , 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. The observation 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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