

Highly stable silicon dioxide films deposited by means of rapid thermal low-pressure chemical vapor deposition onto InP

A. Katz, A. Feingold, U. K. Chakrabarti, and S. J. Pearton
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

K. S. Jones
University of Florida, Gainesville, Florida 32611-2066

(Received 24 June 1991; accepted for publication 23 August 1991)

An attempt was made to deposit a high thermally stable silicon dioxide (SiO_2) film onto InP substrates. The films were grown by rapid thermal, low-pressure chemical vapor deposition (RT-LPCVD), using pure oxygen (O_2) and 2% diluted silane (SiH_4) in argon (Ar) gas sources, in the temperature range of 350–550 °C and pressure range of 3–10 Torr. The SiO_2 /InP structures were heated, post-deposition, up to 1000 °C for durations of up to 5 min, resulting in negligible changes in the properties of the SiO_2 films and a limited SiO_2 /InP interfacial reaction of about 15 nm thick. The higher the initial deposition temperature of the SiO_2 the larger was the film compressive stress and the less the degree of densification the film underwent through the post-deposition heating cycles.

Stability of SiO_2 films during high-temperature thermal cycles is a critical requirement, particularly for use on InP substrates as a part of an electronic or photonic device manufacturing sequence. This is due to the fact that SiO_2 films are used as masks and geometrical aligners for various deposition, implantation, activation, and etching processes, some of which may be performed in temperatures in the range of 600–800 °C. Any changes in the mechanical properties of the SiO_2 film may result in subsequent failure of the manufactured device.

Several techniques have been explored in order to deposit SiO_2 films onto InP substrates, such as plasma enhanced chemical vapor deposition (PECVD),¹ low-pressure chemical vapor deposition (LPCVD),² and irradiation and light assisted CVD.^{3,4} We have recently examined the qualities of SiO_2 films deposited by means of rapid thermal low-pressure chemical vapor deposition (RT-LPCVD). This technique allows for a very short deposition duration at a relatively high deposition rates.

In this letter we report a study of the stability of the RT-LPCVD SiO_2 films through post-deposition heating cycles at temperatures as high as 1000 °C, and duration of 30 s to 5 min. We have evaluated both the mechanical and structural changes that occurred in the film itself, and the SiO_2 /InP interfacial reaction. SiO_2 films were deposited in a low-pressure rapid thermal chemical vapor deposition (RT-LPCVD) A. G. Associates CVD-800™ model reactor.^{5,6} Briefly, this is an horizontal flow, cold-wall, single wafer and load-locked reactor, heated by means of two halogen-tungsten lamp arrays, and capable of processing with inert, hazardous, or corrosive ambients.

The SiO_2 layers were deposited from a gas mixture comprised of pure O_2 and 2% diluted SiH_4 . The gases were let into the chamber and the ambient was stabilized 30 s before the lamps were turned on. The deposition cycles were carried out at a substrate temperature ranging from 350 to 550 °C, durations of about 15 s, and chamber pressures of 7.5 to 9.5 Torr.

The films were rapid thermally sintered *in situ*, post-

deposition, under N_2 ambient at temperatures of 1000 °C for durations of 30 s to 5 min, before being unloaded and analyzed.

Film properties were analyzed in various techniques. Film thicknesses were measured with Rudolph Research Auto El ellipsometer at 632.8 nm wavelength (He-Ne laser), and by a mechanical measurement of chemical etched steps using DEKTAK™ stylus profilometry system. The room temperature IR spectra were recorded within the wavenumber range of 4600–400 cm^{-1} using Fourier transform infrared (FTIR) spectrometry. All the spectra had a signal averaging over at least 400 scans with an instrumental resolution of 3 cm^{-1} . The uncertainty in measurements was within 1 cm^{-1} for the frequency and within 1.5 cm^{-1} in the full width half maximum (FWHM) measurements.

In situ stress measurements were performed using the 2-300 Flexus thin-film stress measurement system. The substrates were measured for their initial curvatures prior to any deposition. The initial curvature was later subtracted from all the following curvature measurements of the corresponding wafers up to 500 °C, a technique which was described in detail elsewhere.⁷

Surface, interface, and morphology analyses were carried out by means of transmission electron microscopy (TEM), both in the plan-view and cross-section modes.

In order to evaluate the stability of the SiO_2 /InP system under high-temperature cycles, we have selected films that were deposited in an optimum condition described in detail elsewhere,⁵ and are represented in Fig. 1. This shows the correlation between the SiO_2 film thickness and the total chamber pressure. For the given deposition conditions, of 10:1, O_2 : SiH_4 gas mixture, deposition temperature of 450 °C and duration of 20 s, a minimum pressure of 4–4.5 Torr is required in order to allow for a film deposition. This dependence was observed for all the grown samples regardless of the deposition temperature.

The stresses in the deposited films were measured *in situ*, for heating up to 500 °C. Figure 2 shows the stress-temperature (σ - T) characteristic of the RT-CVD SiO_2

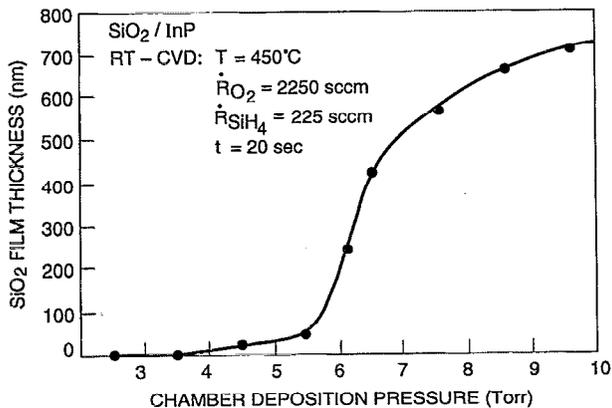


FIG. 1. RT-LPCVD SiO₂ film thickness on InP substrate as a function of the total chamber pressure through deposition at 450 °C, O₂:SiH₄ ratio of 10:1 and duration of 20 s.

films deposited at a pressure of 8.5 Torr at various temperatures of 350, 450, and 550 °C. All the films were deposited with high compressive stresses of -2.1 , -3.1 , and -4.2×10^9 dyne cm⁻², respectively. The higher the deposition temperature, the less plastic deformation was developed in the film through the heat treatment, reflected in the smaller hysteresis in the σ - T graphs. In addition, one can actually define the deposition temperature by following the slope change in the σ - T graphs. This characteristic shows in a clear manner that when exceeding the deposition tem-

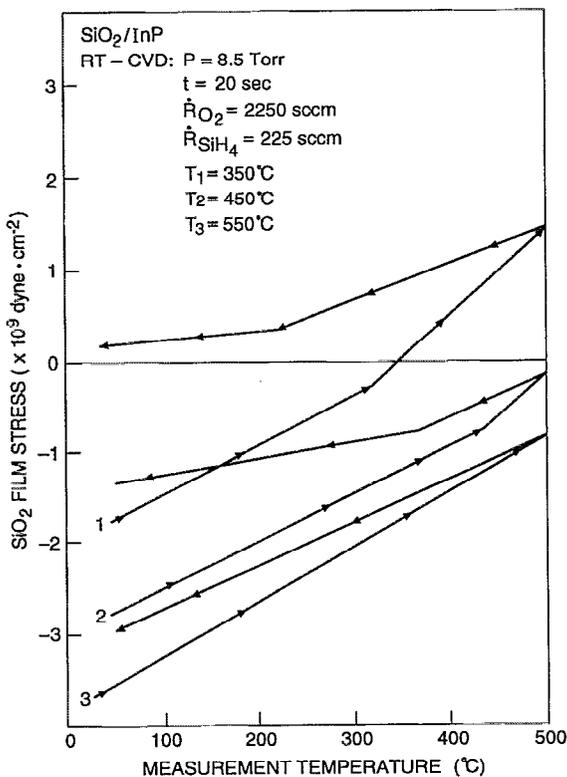


FIG. 2. Stress as a function of RT-LPCVD SiO₂/InP system temperature. The SiO₂ films were deposited at temperatures of 350, 450, and 550 °C, pressure of 8.5 Torr and O₂:SiH₄ ratio of 10:1.

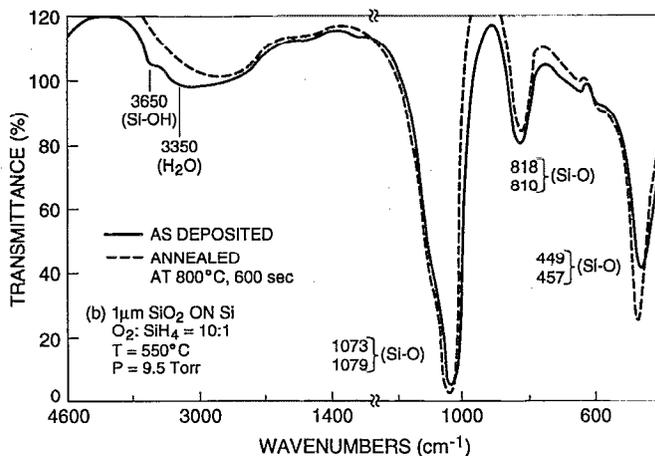


FIG. 3. FTIR transmission spectra of the RT-LPCVD SiO₂ film, deposited at 550 °C, 9.5 Torr and O₂:SiH₄ ratio of 10:1, as deposited and after subsequent annealing at 800 °C for 10 min.

perature during the post-deposition stress measurement heating cycles, the σ - T slope was changed. It can be attributed to the plastic deformation which was developed in the films through the heating cycle and resulted in a more tensile film after cooling back to room temperature. The only film that did not exhibit σ - T slope change was, naturally, the one deposited at 550 °C.

The stability of the SiO₂ film deposited at 550 °C and pressure of 9.5 Torr was examined by means of FTIR, as well. Figure 3 shows the FTIR transmission spectra of the RT-LPCVD SiO₂ film, as-deposited and after heat treatment at 800 °C for 10 min under N₂ ambient. The strongest absorption near 1075 cm⁻¹ and the other two weaker absorptions at 818 and 449 cm⁻¹, all of which are associated with the stretching vibration of the oxygen atoms along the Si-O-Si bond planes,^{8,9} exhibited minor frequency shifts and peak width decreases. The amount of change in these two characteristics, however, are believed to take place as a result of the film densification and not due to changes in the atomic configuration. In addition, a shift of 12 cm⁻¹ in the peak frequency and shrinkage of 11 cm⁻¹ in the half peak width in the vibrational band due to the rocking mode at 449 cm⁻¹ frequency, suggest some minor degree of re-ordering of the amorphous film atomic structure upon sintering.

A further indication of the density or porosity of the films is provided by the intensity of the absorption bands near 3650 cm⁻¹ due to silanol groups and near 3350 cm⁻¹ due to absorbed water.¹⁰ These peaks did not shift as a result of the sintering process, but showed a clear reduction in the intensity, which may be attributed to a partial removal of Si-OH and H₂O groups that were trapped in the deposited film. The morphological changes that took place in the SiO₂ film through the heat treatment, and were detected by means of the FTIR analysis, looked to be relatively minor and were confirmed by means of the density and the stress measurements.

Figure 4 shows high magnification TEM cross-sectional micrographs of the as-deposited RT-LPCVD SiO₂

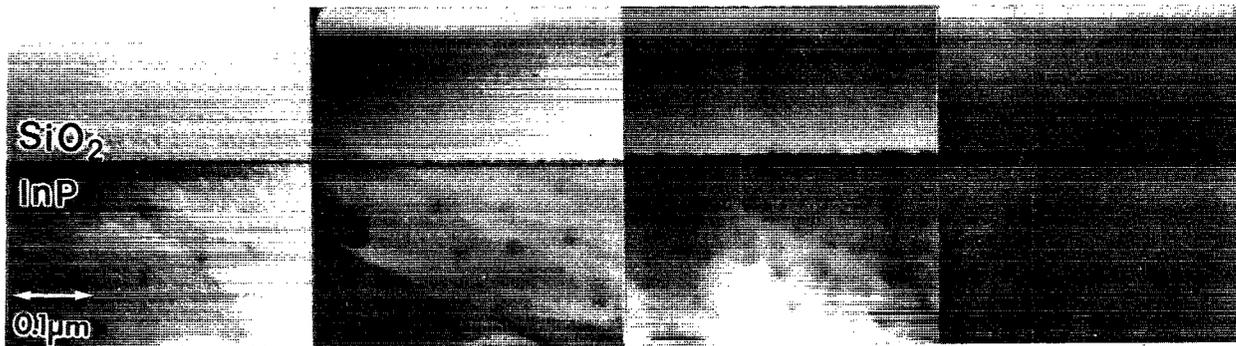


FIG. 4. TEM cross-sectional micrographs of SiO₂ films deposited onto InP substrates at 550 °C, 9.5 Torr and O₂:SiH₄ ratio of 10:1, after post-sintering at 1000 °C for (a) 60, (b) 120, (c) 240, and (d) 300 s.

on InP and after post-sintering at 1000 °C for 60, 120, 240, and 300 s. One can see that in spite of the high-deposition temperature of 550 °C, the SiO₂/InP interface is relatively sharp and featureless, reflecting a damageless deposition process. A limited SiO₂/InP interfacial reaction determined from contrast changes in the TEM was observed in all samples. This data is given, as well, in Figure 5 which presents the interfacial reaction width as a function of the sintering duration. Maximum reaction width of about 12.5 nm, in which the SiO₂ has reacted with the InP, was measured in the sample that was sintered at 1000 °C for 300 s.

Further surface analysis showed that, regardless of the process duration, sintering the SiO₂/InP samples at 1000 °C did not lead to any significant diffusion or reaction process beyond the direct interfacial reaction observed by means of the TEM (see Fig. 4). These results are remarkable in terms of the thermal stability of the RT-CVD SiO₂ films and agree with the FTIR and stress observations regarding the high quality of the film.

In summary, we have demonstrated the morphological quality of RT-LPCVD SiO₂ films deposited onto InP substrates, which was reflected in the extremely high stability of the SiO₂/InP structure through sintering cycles at temperatures up to 1000 °C. This desirable property, complimented by other microstructure and morphological properties, clearly show the potential of the RT-LPCVD SiO₂ film as an excellent candidate for being used as the dielectric material of choice in conjunction with the InP technology.

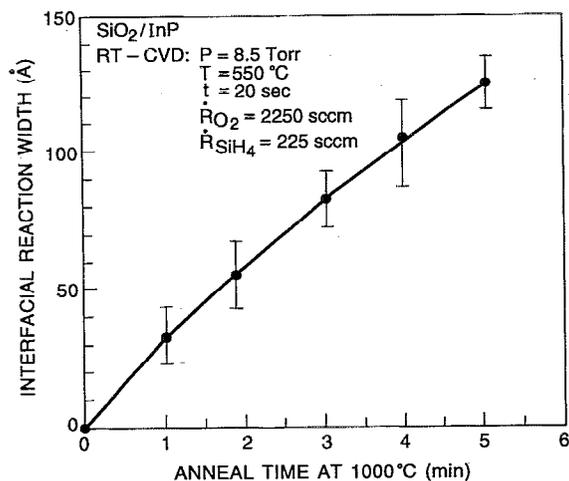


FIG. 5. Interfacial reaction thickness of the InP/SiO₂ system after sintering at 1000 °C, as a function of the sintering duration.

- ¹ K. P. Pande and V. K. R. Nair, *J. Appl. Phys.* **55**, 3109 (1984).
- ² W. Kern and R. S. Rosler, *J. Vac. Sci. Technol.* **14**, 1082 (1977).
- ³ H. Honaka, A. Arai, Y. Fujino, and S. Ichimura, *J. Appl. Phys.* **64**, 4168 (1988).
- ⁴ Y. I. Nissim, J. M. Moison, F. Houzay, F. Leblanc, C. Licoppe, and M. Bensoussan, *Appl. Surf. Sci.* **55**, 1 (1990).
- ⁵ A. Katz, A. Feingold, S. J. Pearton, and U. K. Chakrabarti, *Appl. Phys. Lett.* **59**, 579 (1991).
- ⁶ A. Katz, A. Feingold, S. J. Pearton, U. K. Chakrabarti, and K. M. Lee, *Semicond. Sci. Technol.* (to be published Dec. 1991).
- ⁷ A. Katz and W. C. Dautremont-Smith, *J. Appl. Phys.* **67**, 6237 (1990).
- ⁸ F. L. Galeener, *Phys. Rev. B* **19**, 4292 (1979).
- ⁹ F. L. Galeener and P. N. Sen, *Phys. Rev. B* **17**, 1928 (1979).
- ¹⁰ W. A. Pliskin and H. S. Lehman, *J. Electrochem. Soc.* **112**, 1013 (1965).