

DEPOSITION OF SILICON OXIDE THIN FILMS IN TEOS WITH ADDITION OF OXYGEN TO THE PLASMA AMBIENT: IR SPECTRA ANALYSIS

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Silicon oxide thin films deposited on Si substrates in a RF-plasma CVD reactor, using $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) as the precursor and oxygen as the gas ambient, were studied by IR spectrophotometry. All depositions were performed at a substrate temperature of 200°C, a plasma power of 20 or 80 W and with a DC-bias of -120 V applied to the Si substrate. The observed IR peaks were assigned to corresponding vibrational modes. Peaks related to Si-H, C-H and OH bond vibrations were also detected. Some degree of porosity exists, resulting in a lower refractive index of the films than that typical for SiO_2 material.

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1. Introduction

Silicon oxide films can be produced by different methods, each with advantages and disadvantages for different purposes. Sol-gel [1] and liquid phase deposition [2] do have limitations in terms of the minimal thickness of the films. Sputtering [3] and chemical vapor deposition [4] allow better control of the film thickness, and doping of the films can easily be achieved by adding gases during the deposition process. Vibrational spectroscopy is an important tool for investigating the film properties. Infrared (IR) spectral analysis has been applied to get information on the structure and chemical bonds of Si-containing thin films and alloys [5].

In this paper, we present the results of an IR study of silicon oxide films deposited by plasma enhanced CVD. The influence of deposition parameters such as the plasma power and oxygen gas flow rate on the vibrational properties of the resulting silicon oxide films is considered.

2. Experimental details

The silicon oxide films were deposited onto double-sided polished Si wafers in a downstream plasma reactor (see Fig. 1). The plasma was coupled inductively by a rf generator, working at 13.54 MHz and at powers of 20 and 80 W. Oxygen, at flow rates of 2 or 10 sccm, was used as the plasma gas, and the $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) precursor was introduced to the reactor through a nozzle near the substrate. The resulting total pressure in the reactor was 10^{-2} mbar. The substrates were heated to 200 °C by a resistive heater, and during the deposition a DC-bias voltage of -120 V was applied to them.

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The film materials were examined by infrared spectroscopy using a Bruker Vector 22 spectrophotometer in transmission mode. The refractive indices of the films were determined from ellipsometric measurements performed on a Rudolph ellipsometer in spectral range 300-820 nm. In order to determine the physical composition of the films, their structures were considered as heterogeneous material with optically identifiable regions of amorphous silicon and silicon dioxide, $\text{Si}_x(\text{SiO}_2)_{1-x}$, where x is the atomic fraction. In the modelling, the Bruggeman effective-medium approximation (BEMA) theory [6] was applied and literature data [7] were used for the optical constants of a-Si and SiO_2 .

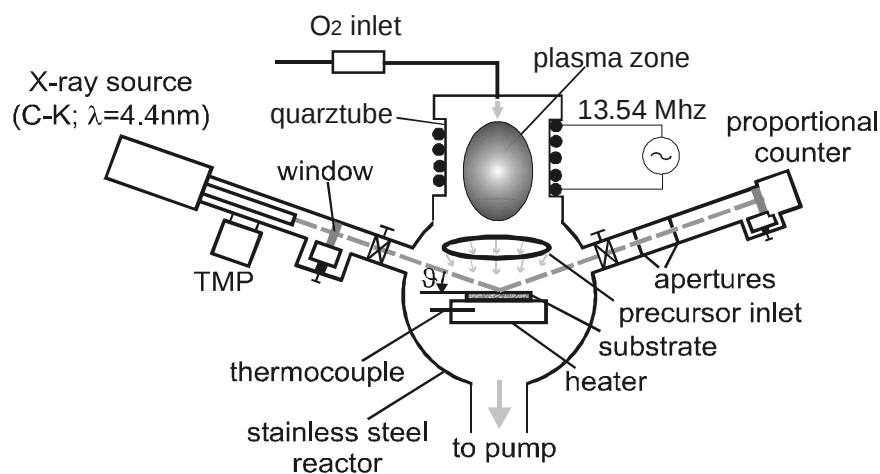


Fig. 1. RF reactor for the plasma-assisted CVD process with in-situ reflectivity measurements.

3. Results and discussion

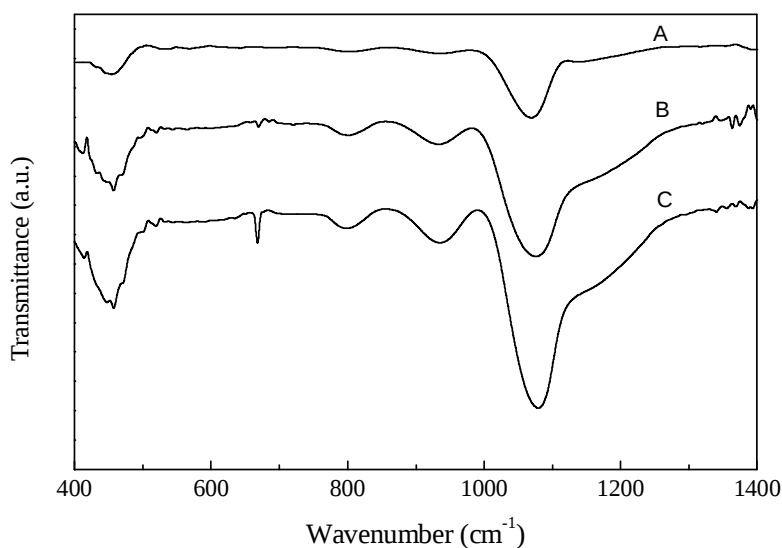


Fig. 2. IR spectra of oxide films deposited under different conditions: A - a power of 80 W and an oxygen flow of 2 sccm; B - a power of 80 W and an oxygen flow of 10 sccm; C - a power of 20 W and an oxygen flow of 10 sccm.

The IR transmittance spectra of the deposited films, in the region characteristic of the Si-O vibrational bands are shown in Fig. 1. They are very similar, thus indicating similar chemical compositions and structures. The overall higher intensity in the IR spectra for the B and C samples is due to the larger film thicknesses. The assignment of the IR vibrational bands in the spectra of the films deposited at different plasma conditions are summarized in Table 1.

As seen from Fig. 1, the IR spectra show characteristic vibrational bands at 1080, 800 and 450 cm^{-1} , corresponding to the stretching, bending and out of plane deformation of Si-O bonds, respectively. The position and shape of the main Si-O vibrational band at 1080 cm^{-1} , and the well-pronounced shoulder suggest a stoichiometric silicon dioxide structure. However, impurity-related bands are also observed.

In the IR spectra small peaks, not shown in Fig. 1 but included in Table 1, are found in the spectral range 1300 to 1500 cm^{-1} . These peaks could be attributed to vibrations of carbon impurity atoms in the films [5,8]. In a similar spectral range, peaks of deformation modes of the $(\text{CH}_m)_n$ C/Si groups ($m=1, 2, 3$; $n=1, 2, 3$) have been detected in sputtered silicon carbon films [9]. Obviously, the oxygen content in the deposition gas is not enough to burn out the carbon from the decomposed TEOS. In the spectra of samples B and C, well-pronounced vibrational bands appear as doublets at 2350 and 2390 cm^{-1} . The intensities of these increase with the amount of oxygen in the reactor. These features could be related to Si-C triple bonds in the stretching mode. An alternative explanation could be the vibration of Si-H bonds in $\text{O}_x\text{Si-H}$ configurations. It is suggested that large amounts of hydrogen related species are also introduced into the growing films, yielding vibrational bands in this spectral region [5]. Within the range 2200 to 2500 cm^{-1} , the vibration of a silicon atom bonded with one or more hydrogen atoms in the Si-H stretching mode has been detected in hydrogenated silicon [8]. In addition, for samples B and C, a strong band at 940 cm^{-1} and a large and very broad peak centered at 3380 cm^{-1} are observed. These correspond to the stretching vibrations of Si-bonded and H-bonded hydroxyl groups, respectively [5].

Table 1. Assignment of the vibrational bands in the IR spectra of silicon oxide films deposited up to a thickness of t_{ox} under different plasma conditions.

Vibrational modes of the chemical bonds	Sample A ($t_{\text{ox}}=100$ nm) Power of 80 W; O_2 flow of 2 sccm	Sample B ($t_{\text{ox}}=520$ nm) Power of 80 W; O_2 flow of 10 sccm	Sample C ($t_{\text{ox}}=380$ nm) Power of 20 W; O_2 flow of 10 sccm
Si-O out of plane deformation	450 cm^{-1} strong band with superimposed small peaks	450 cm^{-1} strong band with superimposed small peaks	450 cm^{-1} strong band with superimposed small peaks
Si-H wagging	670 cm^{-1}	670 cm^{-1}	670 cm^{-1}
Si-O bending	-	805 cm^{-1}	800 cm^{-1}
Si-OH stretching	940 cm^{-1} weak band	940 cm^{-1} strong band	940 cm^{-1} strong band
Si-O-Si stretching	1070 cm^{-1}	1080 cm^{-1} with well pronounced shoulder	1080 cm^{-1} with well pronounced shoulder
Si-OH ; C-H deformation	1300-1500 cm^{-1} superimposed small peaks	1300-1500 cm^{-1} superimposed small peaks	1300-1500 cm^{-1} superimposed small peaks
Si-C triple bonds in stretching mode	2350-2390 cm^{-1} weak double maximum	2350-2390 cm^{-1} strong double maximum	2350-2390 cm^{-1} strong double maximum
HO...H OH stretching	-	3400 cm^{-1} and small peaks in 3600-3700 cm^{-1}	3400 cm^{-1}

The refractive indices of the three kinds of film are smaller than that of stoichiometric SiO_2 material [7]. This is illustrated in Fig. 3, where the spectral dependence of the refractive index of samples A and C, as well as the refractive index of stoichiometric, thermally grown SiO_2 are shown. From the ellipsometric data, modelling the physical composition of the films were performed. The results showed a slightly under-stoichiometric composition, of $\text{SiO}_{1.985}$ for the sample A and $\text{SiO}_{1.938}$ for sample C. Increasing the oxygen flow rate to 10 sccm, however, leads to the appearance of voids with a volume fraction $\sim 2\%$. This result, combined with the IR indication of the presence of water in the film (see Table 1) explains the observed lower values of the refractive index.

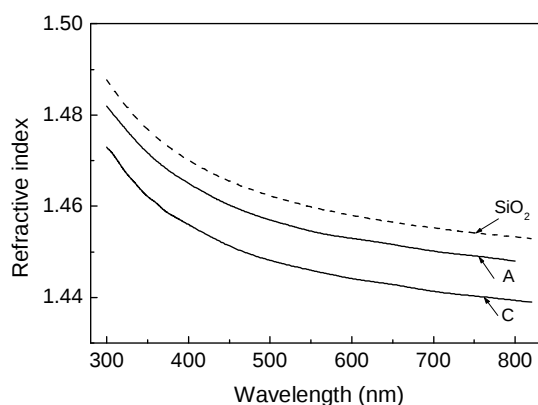


Fig. 3. Refractive index dispersion of silicon oxide films deposited under the different plasma conditions given in Table 1. The refractive index dependence of stoichiometric SiO_2 is inserted.

4. Conclusions

The IR and SE spectra analyses have shown that plasma-assisted CVD deposition using a TEOS precursor yields stoichiometric but less dense silicon dioxide films. The incorporation of carbon and hydroxyl groups in different bond configurations is detected, which suggests the need to increase the oxygen content during film deposition.

References

- [1] J. J. Perez-Bueno, R. Ramirez-Bon, Y. V. Vorobiev, F. Espinoza-Beltran, J. Gonzales-Hernandez, *Thin Solid Films* **379**, 57 (2000).
- [2] M. P. Houn, Y. H. Wang, C. J. Huang, S. P. Huang, J. H. Horng, *Solid-State Electronics* **44**, 1917 (2000).
- [3] K. K. Sion, J. Pinel, V. Dolle, L. Pichon, O. Bonnard, *Microelectronics Engineering* **28**, 459 (1995).
- [4] A. R. Barron "CVD of Insulation Materials" in: *CVD of Nonmetals*. W.S. Reese (Ed.), VCH Weinheim, 1996, 276.
- [5] D. M. Back "Fourier transform infrared analysis of thin films" in *Physics of Thin Films, Thin Films for Advanced Electronic Devices*, Eds. M. H. Francombe, J. L. Vossen, Academic Press, 1991, Vol. **15**, pp 265-309 and references therein.
- [6] D. A. G. Bruggemann, *Ann. Phys. (Leipzig)* **24**, 636 (1935).
- [7] E. D. Palik, editor, "Handbook of Optical Constants of Solids", New York, Academic Press, 1994.
- [8] L. Laura, T. Crowell, J. E. Crowell, L. Logan, *J. Vac. Sci. Technol. A*, **9**, 1002 (1991).
- [9] H. Rubel, B. Schroder, W. Fuhs, J. Krauskopf, T. Rupp, K. Bethge, *phys. stat. sol. (b)*, **139**, 131 (1987).