

DIELECTRIC BREAKDOWN OF SiO₂ THIN FILMS DEPOSITED BY ION BEAM INDUCED AND PLASMA ENHANCED CVD.

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INTRODUCTION

Silicon dioxide in the form of thin films is a very interesting material for electronic, optical or passivation layer applications [1-3]. For many of these purposes, in particular microelectronics, it is critical that compact layers of SiO₂ can be obtained at low temperature. However, most of the established methods of preparation are based either on thermal CVD, requiring in this case very high temperatures, or on plasma CVD. When working at low temperature, the microstructure of the film is usually not sufficiently good and the composition is not well defined. In practice, plasma-activated procedures of preparation of SiO₂ thin films with optical or electronic applications yield optimal microstructures at intermediate temperatures of the order of 200-300 °C. [4-5]

This paper presents a comparative study of SiO₂ thin films prepared at room temperature by ion beam induced chemical vapor deposition (IBICVD) and plasma enhanced chemical vapor deposition (PECVD) methods. The films are characterized by AFM, TEM, RBS, ERDA, NRA, X-ray reflectometry and spectroscopic ellipsometry. While the films prepared by IBICVD are very compact and dense and have a high refractive index ($n = 1.48$ at $\lambda = 550$ nm), those prepared by PECVD exhibit a lower refractive index value ($n = 1.45$ at $\lambda = 550$ nm) lower density and have a higher surface roughness. Films prepared by IBICVD presents a breakdown electric field value (49.14 MV/cm), four times higher than that of the films prepared by PECVD (12.11 MV/cm) and other SiO₂ materials reported in the literature. This higher value is a consequence of the low roughness and high density of the IBICVD films. This type of microstructure is produced by the effect of the highly energetic ion beams (e. g. 400 eV) impinging on the surface of the growing films during their preparation.

Experimental

SiO₂ thin films have been prepared at room temperature by two activated CVD processes: IBICVD and PECVD. In both cases Si(CH₃)₃ Cl has been used as

volatile precursor of Si. The first method consists of the decomposition of the precursor on the surface of the different substrates by the action of a beam of accelerated O₂⁺ ions. A full account of this method has been reported previously [6].

PECVD deposition was carried out by using an external microwave ECR source (SLAN) operated at 400 Watts. A full description of the characteristics of this source can be found in ref [7].

Fourier Transform Infrared (FT-IR) spectra were collected in transmission at normal geometry in a Nicolet 510 spectrometer.

Transmission electron microscopy (TEM) analysis was performed with a Philips CM200 microscope working at 200 kV. KBr substrates were used for conventional TEM examination.

Atomic force microscopy (AFM) images were obtained in air using a Topometrix Explorer microscope working in the non-contact mode.

Spectroscopic ellipsometry analysis were performed using a SOPRA commercial-available system. For the transparent films studied (extinction coefficient $k=0$), the analysis procedure consists in a regression using a Cauchy law to simulate the refractive index $n(\lambda)$ of the layer.

X-ray reflectometry spectra were collected with a special set-up using the angle-resolved dispersive mode with a position-sensitive proportional counter. The technique is able to determine the thickness and density of thin layers.

Rutherford Backscattering spectroscopy (RBS) and Elastic Recoil Detection Analysis (ERDA) measurements of the films were performed in the Ion Accelerator ARAMIS (Orsay, France) using 1.5 MeV He⁺ and 3 MeV He²⁺ particles, respectively. The energy resolution of the detector used in the RBS measurements was 15 keV and 45 keV in the ERDA

measurements. RBS and ERDA spectra were simulated using the RUMP code.

Breakdown voltages have been obtained through a voltage ramp with a constant slope of 20 V/s by using the experimental arrangement shown in Fig.1. This voltage was applied separately to Au contacts of diameter 1mm evaporated on the sample surface.

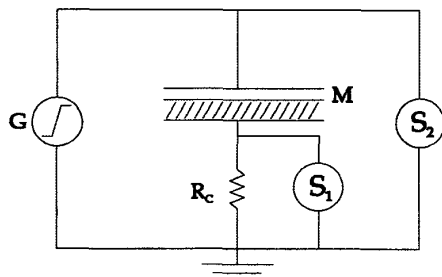


Figure 1. Experimental arrangement used to measure breakdown electric field and charge to breakdown: function generator, G, with his load resistor, R_c , thin film sample, M, and oscilloscope probes, S_1 and S_2 .

The function generator G is able to generate voltages up to 400 V, with 100 mA of maximum current, and to perform ramps of slopes ranging from 20 V/s to 10^6 V/s with 2% of output ripple. The system is based on a switching DC power supply (flyback converter), controlled by a computer (on-board microcontroller).

Output voltage waveform is generated by the microcontroller using a stored data pattern, with a sampling interval of 0.1 ms. Stored data pattern can be modified at any time by computing a new pattern with the on board microcontroller (only ramps are allowed), or by down loading a new pattern from an external host computer, using the on-board RS232 port. In the latter case, any voltage shape complying the restrictions mentioned above can be performed. As an added value, the system is able to store the real output voltage which can be downloaded back to the host computer for analysis (study of dielectric breakdown). This makes unnecessary the presence of additional elements, e.g. oscilloscopes.

S_1 and S_2 are digital oscilloscope probes in single trigger mode. S_2 measures the applied voltage to the sample, M, and S_1 the voltage in a load resistance of $1k\Omega$ in order to calculate the current through the sample at any time. Both signals can be stored by means of a HP-VEE software for their later study.

In Figure 2, we show the current variation as well as the applied voltage ramp at a particular Au contact for a IBICVD sample. From both we can obtain the values of breakdown electric field and, by numerical integration, of the charge to breakdown.

A particular suited distribution, namely extreme value statistics, was used to calculate the intrinsic breakdown and charge to breakdown of the sample[8-9].

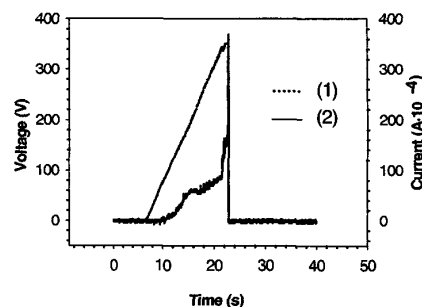


Figure 2. Electric signals from a particular Au contact in a IBICVD sample: (1) applied voltage ramp; (2) current variation.

Results and Discussion

The composition of the thin films prepared by either IBICVD or PECVD was determined by a combined RBS/NRA analysis. They are formed only by Si and O atoms. The obtained O/Si stoichiometry were 2 ± 0.02 in all samples.

SiO_2 composition at the surface was also obtained by XPS. Some carbon was

detected that was readily removed by mild Ar^+ or O_2^+ bombardment. This carbon is the contamination of the samples by exposure to air.

The content of H in the samples was determined by ERDA measurements. The H/Si ratio was less than 0.25 and 0.35 for ion and plasma films, respectively. These values are similar or lower than those reported in the literature for SiO_2 thin films prepared by thermal or plasma CVD [10]. It is also shown below by FT-IR analysis that the concentration of -OH groups is higher in PECVD- SiO_2 than in IBICVD- SiO_2 films, a feature that can be explained by the rougher microstructure of these films.

Figure 3 shows topographic AFM images of the surface of SiO_2 films approximately 100 nm thick prepared by IBICVD and PECVD. The images, presented within the same current scale, clearly indicate that the IBICVD- SiO_2 sample has lower surface roughness. The root mean square (RMS) surface roughness values deduced from the AFM images are 0.21 and 1.5 for the IBICVD and PECVD films thus confirming the previous assessment of surface roughness of the samples.

Planar-view TEM images have been obtained for the two types of oxide thin films studied here. The IBICVD-SiO₂ film shows a uniform contrast within the film (homogeneous layer) where no voids are distinguishable. On the other hand, the PECVD-SiO₂ sample, exhibits a contrast with granular structure characterized by agglomerates of ~20 nm that superimpose to form the whole film thickness. This granular structure is related to the higher surface roughness (cf. Figure 3) of these films.

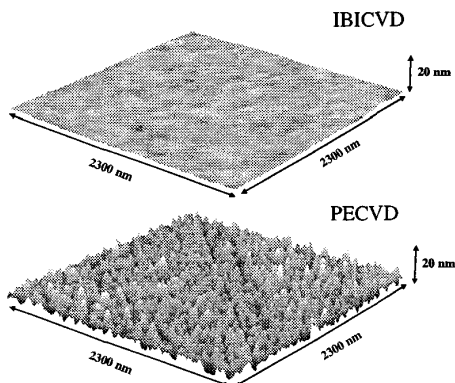


Figure 3. AFM images of the two samples

Information about density and surface and interface roughness of thin films was obtained by X-ray reflectometry. The density of the films was deduced from the total reflectivity angle θ_c , by this procedure, the density for the IBICVD-SiO₂ and PECVD-SiO₂ films were 2.46 and 2.08 g cm⁻³, respectively (the density of bulk silica is 2.20 g cm⁻³).

For the IBICVD film, the absence of an interference pattern in the reflectometry spectra (not shown) could be related to a not well defined interface between the film and the substrate. This may seem contradictory with the low surface roughness determined by AFM for this sample. However, a rough substrate/film interface is expected owing to the fact that O₂⁺ ions of relatively high energy (i.e. 400 eV) are used for the deposition of the films. Based on TRIM calculations [11], a penetration depth of 1.5-2.0 nm is expected for these oxygen ions. Oxygen diffusion through the Si substrate could be an additional reason for the absence of interference fringes.

The hypothesis of a poorly defined film/substrate interface was checked by high resolution TEM (HRTEM) cross-section observation of the interface. The film/substrate interface in the latter sample is well defined, having a thickness smaller than 1.2 nm for the whole observation area. In fact, the well ordered structure of the Si single crystal substrate, characterized by an ordered arrangement of points, gives rise abruptly to the homogeneous shadowed structure typical of amorphous SiO₂ layer. However, for the IBICVD

samples the interface is less defined, being apparent the superposition of the substrate points with some shadowed zones that indicate the formation of SiO₂/SiO_x (x<2) inclusions within the substrate.

The different microstructure of the two types of samples must yield different physical and chemical film properties. Refractive index $n(\lambda)$, obtained using spectroscopic ellipsometry in the spectral range 0.21 μm-1.2 μm, are presented in Fig 4. One can clearly observe that, for the entire spectral range, the n value for the IBICVD-SiO₂ sample is higher than that measured for the PECVD-SiO₂ layer ($n = 0.03$). The higher refractive index of the IBICVD films agrees with the value of density obtained for this sample by X-ray reflectometry. This refractive index is within the highest values reported in literature for SiO₂ thin films prepared by different methods [12].

The previous results have shown that SiO₂ thin films prepared by IBICVD are more compact and dense than those prepared by PECVD. Main factor for this enhanced compaction of the film is the kinetic energy of the impinging ions [13].

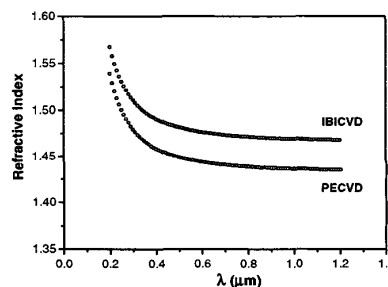


Figure 4. Refractive index vs λ for IBICVD and PECVD samples

For the IBICVD sample (70 nm width of SiO₂ on Silicon) and using the extreme value statistics, a breakdown voltage of $V_b=344$ V was obtained which means a breakdown electric field of $E_b=49.14$ MV/cm. Charge to breakdown is $Q_b=105$ mC. For the PECVD sample (140 nm width of SiO₂ on Silicon) the corresponding values are $V_b=169.6$ V, $E_b=12.11$ MV/cm and $Q_b=73.13$ mC.

CONCLUDING REMARKS

The previous results have clearly illustrated the importance of ballistic interactions of impinging particles for an enhanced compactness of SiO₂ films. This enhanced compactness leads to a modification of their physical properties as for example the refractive indices (cf. Fig. 2), which is of great interest for microelectronic and optical applications. It is also

worth to mention that ion beams might be also used for a selective deposition of the films according to a lithographic technique. In fact, deposition by IBICVD occurs at room temperature only in the zones where ion beams are impinging on the substrate surface. The use of focused beams rastered according to a given pattern or that of a mask put between a broad beam and the substrate should produce such patterned films of a large interest for microelectronic applications. At present, research is being carried out in our laboratory to explore this possibility of the IBICVD procedure.

This paper has also shown that a broad interface develops between the silicon substrate and the SiO₂ layer grown by IBICVD. A way of minimizing such interlayer thickness could be obtained by depositing an initial SiO₂ thin layer, either by PECVD or lowering the energy of the ion beam to reduce the mixing. Then, the thin film could be grown on the top of this thin layer as it is described in the paper.

BIBLIOGRAPHY

- [1] P Balk Adv. Mater. 7 (1995) 703.
- [2] D.L. Griscom. MRS Bull. Jun-Aug. 20 (1987).
- [3] W Kern, R.S. Rosler. J. Vac. Sci. Technol. 14 (1977) 1082.
- [4] T. Roppel, D.K. Reinhard, J. Asmussen. J. Vac. Sci. Technol. B 4 (1986) 295.
- [5] K. Strater. RCA Rev. Dec. (1968) 618.
- [6] J.P. Espinós, A. Fernández, V. M. Jiménez, J. C. Sánchez-López, L. Contreras, D. Leinen, A.R. González-Elípe. Avd. Mat. CVD 3 (1997) 219.
- [7] F. Werner, D. Korzec, J. Engemann, Plasma Sources Sci. Technol., 3 (1994) 473.
- [8] J.F. Verweij and J.H. Klootwijk, "Dielectric breakdown I: a review of oxide breakdown", Microelectronics Journal, 27, pp. 611-622, 1996.
- [9] V.A. Rozhkov et al., "Electrical breakdown of rare earth oxide insulator thin films in silicon MIS structures", 1995 IEEE 5th Int. Conf. on Conduction and Breakdown in Solid Dielectrics, Leicester (UK), July 10-13, pp. 418-422, 1995.
- [10] R. Etemadi, C. Godet, C. Perrin, J. Bouree, B. Drevillon, C. Clerc. Surf. Coat. Technol. 80 (1996) 8
- [11] J.F Ziegler, J.P Biersack, U. Littmark, The Stopping and Range of Ions in Solids, Vols I-II, Pergamon, New York. 1986.
- [12] L. Zajčková, J. Janca, V. Perina. Thin Solids Films 338 (1999) 49.
- [13] O. Auciello, R. Kelly (eds). Ion Bombardment Modification of Surfaces. Elsevier Science Publishers B.V., 1986.