Structural Properties of Low Temperature Silicon Oxide Films Prepared by Remote Plasma-Enhanced Chemical Vapor Deposition

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ABSTRACT

High structural quality silicon dioxide films have been prepared by the remote plasma-enhanced chemical vapor deposition technique using silicon tetrachloride and oxygen as source materials, at substrate temperatures lower than 200° C. In addition to the source gases, hydrogen was fed into the deposition chamber. The role of the H₂ gas is to react with the chlorine from the SiCl₄ decomposition forming HCl vapor which is removed from the deposition chamber. The role variations in the substrate temperature, plasma power and oxygen, hydrogen, silicon tetrachloride, and argon flow rates have on the oxide quality are analyzed. The samples were characterized by IR spectroscopy, ellipsometry, chemical etch rate, and Auger electron spectroscopy (AES) measurements. Silicon dioxide films of suitable quality have been prepared at substrate temperatures as low as 50°C. Samples prepared at this temperature with low deposition rates show good oxide.

There is increasing interest in the deposition of silicon dioxide films prepared at low substrate temperature for electronic device applications.^{1,2} Recently, the possibility of preparing electronic grade SiO₂ thin films by plasma-enhanced chemical vapor deposition (PECVD) has been reported³ and also by remote plasma-enhanced chemical vapor deposition (RPECVD),4 at relatively low substrate temperatures (T_s) with structural and electrical properties similar to those obtained by thermal CVD at higher T_s . In general, a mixture of silane (SiH₄) and either N_2O and O_2 has been used and these gases must be diluted with argon and/or helium to avoid incorporation of hydrogen in the deposited films. The preparation of silicon dioxide films using SiCl₄ and O₂ or SiF₄ and N₂O as source materials for the PECVD technique has been reported.5,6 However, the substrate temperature used in those cases was $\geq 200^{\circ}$ C to produce thin films without hydrogen or water-related impurities and with good structural properties. In the PECVD process, all the gases are exposed to the plasma and the substrate is immersed in the plasma. Meanwhile, in the RPECVD process only a subset of the reactant gases is directly plasma excited and the substrate is outside of the plasma region. These restrictions limit the reaction pathways leading to film deposition. We report here the structural properties of silicon dioxide films deposited by RPECVD as a function of the deposition parameters. The source gases used were silicon tetrachloride and oxygen. In particular the deposition rate, chemical wet etch rate, refractive index, location of the stretching vibration of the Si-O bonds, composition analyses, and depth distribution profiles are analyzed as a function of the deposition parameters.

Experimental

The deposition chamber used here is shown in Fig. 1. In the RPECVD technique only a portion of the process gas is fed through the plasma region, and here this portion is formed by argon and oxygen. The other part, formed by silicon tetrachloride and hydrogen, is fed directly to the substrate region. The excitation of the gas delivered through the plasma region was achieved by capacitively

coupling with an RF power generator. The deposition parameters varied were: substrate temperature (T_s) , the plasma power (W), the oxygen flow rate (F_0), the silicon tetrachloride flow rate (F_{sc}) , and the hydrogen flow rate $(F_{\rm H})$. The silicon tetrachloride vapors were obtained from a liquid source kept at room temperature. Table I shows the range of variations for the above-mentioned deposition parameters. The chamber deposition pressure was kept constant in all cases at 400 mTorr with a throttle valve coupled to a baratron pressure sensor. The chamber was evacuated predeposition to a base pressure lower than 10⁻⁵ Torr with a turbomolecular pumping system. The gas flow rates and deposition pressure are such that the flow of gas molecules back into the plasma region from other parts of the deposition chamber is minimized.⁷ The oxide films were deposited on crystalline p-type silicon wafers with a (100) orientation and 200 Ω -cm electrical resistivity. The IR transmittance characteristics were obtained with a phase Fourier transform spectrophotometer in a wavelength range from 400 to 4600 cm⁻¹. The thickness and refractive index (n) of the films were measured with a commercial ellipsometer using the 630 nm line from a He-Ne laser. The chemical wet etch rate in P solution [15 parts hydrofluoric



Fig. 1. Schematic diagram of the dielectric deposition chamber. There is a capacitive coupling.

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Table I. Variation ranges for the deposition parameters.

Substrate temperature (T_s)	25 to 200°C
Plasma power (W)	10 to 50 W
Oxygen flow rate (F_0)	2.2 to 7.7 sccm
Silicon tetrachloride flow rate (F_{sr})	0.8 to 2.0 sccm
Hydrogen flow rate $(F_{\rm H})$	0.0 to 12.4 sccm

acid (49%), 10 parts nitric acid (70%), and 300 parts deionized water]⁸ was obtained by measurements of the thickness of the film before and after the chemical etch. A scanning Auger microprobe (Perkin-Elmer PHI-595) equipped for AES and scanning electron microscopy was used for the surface analyses and depth distribution profiles measurements. The background pressure was 2×10^{-10} Torr, the electron beam energy was 3 keV, and a current of 100 nA was used to avoid as much as possible any radiation damage.9 The electron beam can be focused down to a diameter of about 50 nm and rastered. Data acquisition and analysis were accomplished with a physical electronics multiple technique analytical computer system. The Auger electrons were collected with the cylindrical mirror analyzer with an energy resolution of 0.5% and were recorded digitally in the $E^*N(E)$ mode. The energy increment was 0.5 eV and the signal was averaged over many energy sweeps. The $E^*N(E)$ spectra were sequentially smoothed and differentiated with respect to energy by 11-point and three-point spline routines, respectively. Sputtering for composition and depth profiling was performed with a 2 keV Ar ion beam, also to avoid induced damage.

Results

The results of the structural characterization show that there is no clear trend for the dependence of the Si-O stretching mode (SM) vibration with the variations in the deposition parameters. The resolution of the IR spectrophotometer is 4 cm⁻¹, constant in the range analyzed. Nevertheless, for the lowest substrate temperature used, the SM is located at 1076 cm⁻¹, which may indicate a porous material. A similar behavior can be observed for the lowest hydrogen flow rate samples. However, in most cases the SM vibration is located at wavelengths lower than 1070 cm⁻¹. This fact may indicate that the deposited films are formed by a slightly silicon-rich material.¹⁰

Figure 2 shows the IR spectra for samples OS222, with $F_{\rm H} = 0$ sccm (Fig. 2a), and OS225, with the highest hydrogen flow rate $F_{\rm H} = 12.4$ sccm (Fig. 2b). These spectra show the effect of the hydrogen flow rate. When $F_{\rm H}$ is zero there are peaks located at 425 and 625 cm⁻¹ which may be associated with chlorine radicals SiCl₃ and SiCl₄, respectively, incorporated in the deposited films.¹¹ Meanwhile for the highest $F_{\rm H}$ used the peaks associated with chlorine impurities are small. SiO-H related peaks are shown in the spectrum of the sample OS222.

The refractive index does not show clear trends with some of the deposition parameters, although in general it acquires values in the range from 1.465 to 1.473 which are higher than that of the stoichiometric compound (1.460). This behavior indicates that the prepared films may be formed by slightly silicon-rich material, which is in agreement with the location of the SM vibration. Although there is another possibility which is associated with the built-in stress in the films that results in slightly lower stretching frequency and slightly higher refractive index.^{12,13} The refractive index increases as the substrate temperature increases, similarly *n* increases as a function of the hydrogen flow rate. The lowest values for *n* (1.45) are associated with the lowest T_s and F_H , indicating porous materials.

Figure 3 shows the dependence of the deposition rate (R_d) and the etch rate (R_e) on the substrate temperature. In all cases the gas flow rates were kept constant at $F_o = 4.9$ sccm, $F_{sc} = 1$ sccm, $F_H = 9$ sccm, and the plasma power was W =30 W. The deposition rate is almost constant while the T_s variations and R_e decrease as the substrate temperature increases. Figure 4 shows the dependence of R_d and R_e with the silicon tetrachloride flow rate. The other gas flow rates had the same values indicated above and $T_s = 50^{\circ}$ C. In gen-



Wavenumber (cm⁻¹)

Fig. 2. IR spectra of samples (a) OS222 with $F_{\rm H}$ = 0 sccm, and (b) OS225 with the highest hydrogen flow rate used, $F_{\rm H}$ = 12.4 sccm.

eral, R_d increases as a function of F_{sc} and R_e decreases, at first abruptly, as F_{sc} increases. For $T_s = 50^{\circ}$ C, W = 30 W, $F_{sc} =$ 1 sccm, and $F_H = 9$ sccm, the deposition rate and the etch rate decrease as F_o increases as is shown in Fig. 5. Figure 6 shows that when the hydrogen flow rate increases, R_d and R_e decrease. In this case the other deposition parameters were fixed at $T_s = 50^{\circ}$ C, W = 30 W, $F_{sc} = 1$ sccm, and $F_o =$ 4.9 sccm. Under these same conditions except W and with $F_H = 9$ sccm, Fig. 7 shows the behavior of R_d and R_e as functions of the plasma power. In this case, also, both properties increase as the plasma power increases. In all the studied cases the argon flow rate was kept constant at $F_A =$ 40 sccm.

The AES spectra were performed on the surface of the samples and on the interface between the silicon substrates and the deposited films. Also, concentration profiles were taken for all the studied samples. Figure 8 shows the AES spectra at the surface (Fig. 8a) and on the interface (Fig. 8b) for the sample with $F_{\rm H} = 0$ sccm. Figure 9 shows the depth distribution profile for the sample OS210, for the lowest oxygen flow rate $F_{\rm O} = 2.2$ sccm. The AES spectra at the



Fig. 3. The deposition rate (\odot) and the P solution etch rate (\bigcirc) as functions of the substrate temperature.



Fig. 4. Dependence of the deposition rate (\bullet) and the etch rate (\bigcirc) on the silicon tetrachloride flow rate.

surface of the films show a peak at 76 eV associated with oxidized silicon and a peak located at 512 eV related to oxygen. In these spectra there are no peaks associated with chlorine (180 eV) or with unoxidized silicon (89 eV). The carbon peak (273 eV) may be due to surface postdeposition contamination. The AES spectra at the interfaces show only a well-defined peak due to metallic silicon from the substrates. There is a small signal related to oxygen at 512 eV. Also, there is no signal related to chlorine. Similar behavior is shown by all the other samples analyzed. In general, the depth distribution profiles show that the oxygen and silicon acquire values of about 60 and 30 atomic percent (a/o), respectively, and the depth distribution is uniform. This condition may indicate a composition near to that of a stoichiometric material (Si/O = 0.5).

Discussion

The IR spectrum of sample OS222 (Fig. 2a), which was prepared without a hydrogen flow, shows well-defined peaks for the stretching (1070 cm⁻¹), bending (810 cm⁻¹), and rocking (450 cm⁻¹) mode vibrations of the Si-O bond. It also shows a broad peak located at 940 cm⁻¹ possibly related to water or silanol (SiOH) impurities,¹² which may be from diffusion after film deposition. There are peaks located at about 625 and 425 cm⁻¹ associated with silicon chloride radicals, SiCl₂ and SiCl₃, respectively.^{11,14,15} Meanwhile, in the spectrum from the sample OS225 besides the peaks due to the Si-O bond, there are only small peaks due to silicon chloride radicals at 650 and 425 cm⁻¹. These spectra show that the effect of the hydrogen flow may be explained if the purpose of adding hydrogen to the deposition



Fig. 6. The R_d (\bullet) and R_e (\bigcirc) variations as functions of the hydrogen flow rate.

chamber was to remove chlorine generated by the SiCl₄ molecules decomposition. When $F_{\rm H}$ is zero, chlorine is not removed efficiently from the chamber, and it has a higher probability for incorporation in the deposited film. At the highest hydrogen flow, peaks related to Si-Cl bonds are still present although smaller in magnitude. This result may indicate that the highest $F_{\rm H}$ used was not sufficient for removal of all the chlorine produced during the process.

The increase of the refractive index with the increase of the substrate temperature may be explained considering that at higher T_s the species impinging on the substrate surface has a higher lateral mobility which may produce a film with higher density than those deposited at low T_{s} . The refractive index also increases with the hydrogen flow rate. This behavior is associated with a gettering type of action of the hydrogen, which reacts with the chlorine from the SiCl₄ generated species, avoiding the incorporation of SiCl_x radicals in the deposited films. In the general PECVD process the deposition rate of the deposited films increases as the substrate temperature increases,¹⁶ but here the rate is almost constant with the variation of T_s . This result indicates that the substrate temperature for this technique does not have an active role in the generation of deposition precursors. These precursors should be generated in the plasma region and near the substrate surface due to the argon metastables (Ar') transported from the plasma region. This possibility is suggested by the dependence of the deposition rate with the plasma power. As the plasma power is increased, the argon and molecular oxygen (O'_2) metastable concentrations in the plasma increase. This increase results in a more efficient decomposition of the SiCl₄ and H₂ molecules at the substrate surface region, and then



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Fig. 8. Auger electron spectra of sample OS222, with $F_{\rm H} = 0$ sccm, (a) on the surface, and (b) at the interface.

many deposition precursors are produced which react with the O'_2 giving a high deposition rate. For high silicon tetrachloride flow rates the deposition rate also increases. This behavior is explained if we consider that more SiCl₄ molecules result in more deposition precursor species. The decrease of the deposition rate with increasing flow rates of hydrogen and oxygen is not understood at present. It is likely, however, that a competitive process to the deposition of the oxide takes place as the flows of these gases are increased. Figure 3 indicates that the substrate temperature is not important for the deposition rate, but it has a strong effect on the etch rate. The lateral surface mobility



of the adsorbed species is higher at higher T_s in such a way that it results in a better accommodation coefficient. Thus, for a constant rate of impinging species, films with density near to that of a bulk sample are produced at $T_s \ge 150^{\circ}$ C. The increase in the hydrogen flow rate results in a decrease of the etch rate; for higher $F_{\rm H}$, more atomic hydrogen may be generated which reacts with chlorine resulting in lower incorporation of Cl in the films. It is well known that the SiO₂ etch rate in the P solution has a value of 2 Å/s. Considering the selectivity of the P etch solution,⁸ chlorine incorporated in SiO₂ may result in chemical etch rates higher than that of the stoichiometric material. In this way as the chlorine concentration incorporated in the film decreases the chemical etch rate may decrease to a value closer to that of silicon dioxide. Meanwhile, a higher oxygen flow rate increases the probability of producing a higher concentration of oxygen metastables, which may result in a deposited film with a composition near to the stoichiometric SiO₂ (lower etch rates). Also, higher plasma power results in more O₂ and Ar' transported from the plasma region. This result may produce reactions in the gas phase resulting in the formation of defective films with refractive index and etch rates corresponding to porous materials.

The AES spectra in Fig. 8 shows only signals associated with oxidized silicon at 76 eV and oxygen at 512 eV. There is no signal (at 180 eV) due to chlorine incorporated in the films. The conditions of the argon ion beam and the excitation electron beam used in the AES measurements were suitable for avoiding induced damage in the samples. The lack of detection of chlorine by AES measurements may indicate that the amount of chlorine present is lower than the detection limit of this technique since its presence is detected by IR spectroscopy. The depth distribution profiles show that the samples have a silicon-to-oxygen ratio close to the one expected for stoichiometric oxide (Si/O = 0.5). In general, the refractive index has slightly higher values than that of the stoichiometric material. However, that there is no signal associated with Si-Si bonds in SiO₂ at 89 eV indicates that this film may be stoichiometric SiO_2 . Thus, the refractive index values, higher than that of stoichiometric material may be associated with built-in stress.^{12,13}

Information related with interface states in these oxides is not included here due to limitation in our characterization equipment and the scope of this paper. However, we acknowledged that this topic is an important aspect that should be addressed.

Conclusion

Good structural quality silicon dioxide films have been prepared by the RPECVD technique using SiCl₄ and O₂ as source materials at substrate temperatures lower than those reported previously using PECVD and RPECVD with silane and nitrous oxide as source gases. The hydrogen flow rate added has a gettering type of action reacting with the chlorine species generated by the SiCl₄ decomposition. This effect eliminates substantial Cl incorporation in the deposited films as is shown by the IR and Auger electronic spectroscopies. In general, samples with low deposition rates show a refractive index in a range from 1.46 to 1.47 which may be due to a slightly silicon-rich material or to the built-in stress in the films. These samples also show lower chemical etch rates. The etch rate values are comparable to those obtained for CVD oxides and are not much higher than those obtained in thermal oxides. The substrate temperature plays no active role in the generation of deposition precursors species, particularly on the deposition rate as is normally observed in the PECVD technique. $T_{\rm s}$ affects, however, the density of the deposited films, as well as does the plasma power.

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Growth of Polycrystalline Diamond over Glassy **Carbon and Graphite Electrode Materials**

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ABSTRACT

Boron-doped polycrystalline diamond thin films were grown over glassy carbon electrode material and POCO graphite by a microwave plasma-assisted chemical vapor deposition (CVD) using a gas mixture of methane and hydrogen. As-de-posited films were analyzed by scanning electron microscopy (SEM) and Raman spectroscopy for their morphology and chemical nature, respectively the diamond films grown over glassy carbon and graphite electrode material may have some use in electroanalysis since the doped diamond films are electrically conductive, erosion resistant, and chemically inert.

Carbon belongs to the fourth group of the periodic table and it exists naturally mainly in two allotropic crystalline forms such as diamond and graphite. Diamond has unusual properties and is particularly chemically inert in various acidic and basic solutions. There are several forms of graphite such as (i) polycrystalline graphite, (ii) natural graphite, (iii) highly oriented pyrolitic graphite (HOPG), etc. There are also several amorphous carbons such as (i)glassy carbon (GC), (ii) diamondlike carbon, (iii) coke, (iv) charcoal, (v) carbon fibers, (vi) various forms of carbon/ carbon composites, etc.¹ These amorphous carbons do not constitute distinct allotropes of carbon since they have varying degrees of bonding disorder and hydrogen content. Fullerenes (buckminsterfullerenes) are considered a third form of carbon.² Fullerenes are molecular forms of carbon, whereas diamond and graphite are infinite periodic networks of solid carbon.

GC, pyrolitic graphite, platinum, dropping mercury electrode (DME), etc., are the materials of general interest for electroanalysis since they all have large usable potential range in acidic solutions.³ GC and other solid electrodes normally are deactivated when they are exposed to electrolyte solutions or to an ambient for a long time. Activation of GC may be regenerated by using several approaches such as mechanical polishing, electrochemical polishing, plasma treatments, heat- or annealing treatments, etc. Fagan et al.⁴ have described the activation of GC electrode using vacuum heat-treatments and the references therein described other activation procedures. To alleviate this

problem an initial study is conducted on the feasibility of doped diamond growth over GC. Ramesham et al. 5-7 have shown that the resistivity of boron (acceptor) doped CVD diamond films (p-type) can be decreased to 1-10 Ω -cm. The resistivity of doped diamond thin films is unchanged when the films are subjected to hydrogen microwave plasma treatment and heat-treatments. Therefore, the resistivity of the films are stabilized. Low resistivity and chemical inertness of doped diamond films may be useful for investigating their application in electroanalysis.

Swain and Ramesham⁸ haa shown recently in their preliminary results that the low resistivity B-doped diamond film grown over silicon electrode has high polarization resistance, low double-layer capacitance, stable electrochemical response over freshly prepared GC electrode material. Pleskov et al.9 have reported photoelectrochemical properties of undoped polycrystalline diamond thin films.

Seteka¹⁰ has reported the data on the consumption rate for the artificial graphite, GC, and diamond with the products of hydrogen microwave discharge at low pressure. The consumption rate for GC and graphite are larger by two orders of magnitude than that of diamond. Typical etch rates observed in a hydrogen microwave plasma (300 W, 920°C, 10 cm³/min, 30 Torr, and 20 h) of graphite, GC, and diamond were 0.13, 0.11, and 0.006 mg/cm²-h, respectively. We have attempted to grow diamond on GC and graphite though their etching rates are higher in hydrogen microwave plasma by two orders of magnitude over diamond. Etched GC and graphite by atomic hydrogen may be acting as a carbon source for the diamond growth in addition to the hydrocarbon introduced intentionally into the reactor

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