Ści., 237, 35 (1990).

- B. B. Pate, *ibid.*, **165**, 83 (1986).
 M. Tsuda, T. Hoshino, S. Oikawa, and I. Ohdomari, *Phys. Rev.*, **B39**, 11241 (1991).
- 17. T. Hoshino, S. Oikawa, M. Tsuda, and I. Ohdomari, ibid., B39, 11248 (1991).
- R. J. Hammers, *Phys. Rev. Lett.*, **59**, 2071 (1987).
 K. Miki, H. Tokumoto, T. Sakamoto, and K. Kajimura, *Jpn, J. Appl. Phys.*, **28**, L1483 (1989).

Low Temperature Deposition of SiO₂ by **Distributed Electron Cyclotron Resonance Plasma-Enhanced Chemical Vapor Deposition**

F. Plais¹ and B. Agius*

Institut Universitaire de Technologie, Université Paris Sud (XI), Plateau du Moulon, BP127, 91403 Orsay Cedex, France

F. Abel and J. Siejka

Groupe de physique des Solides, Universités Paris VI et Paris VII, Tour 23, 2 place Jussieu, 75251 Paris Cedex 05, France

M. Puech and G. Ravel

Alcatel SDG, PAE Les Glaisins, BP69, 74009 Annecy Cedex France

P. Alnot and N. Proust

Thomson-CSF LCR, Domaine de Corbeville, 91404 Orsay Cedex, France

ABSTRACT

Silicon dioxide thin films have been deposited at low substrate temperatures ($T_s < 120^{\circ}$ C) using a microwave plasma. A new type of microwave excitation, the distributed electron cyclotron resonance (DECR), which provides high density plasma ($\approx 10^{11}$ cm⁻³) of low-energy ions, has been used. Pure N₂O and SiH₄ are mixed in the discharge. At constant pressure (0.1 pa), the ratio of N_2O flow to SiH₄ flow (R_0) was varied from 1-9. We have studied the effects of the gas phase composition at two different microwave powers (800 and 1200 W) on the refractive index, atomic composition, infrared absorp-tion bands, etch rate, and electrical properties of the films. For ratio R_0 larger than 4, near-stoichiometric films are obtained, with N and H atomic contaminations below 2 and 5 atomic percent (a/o), respectively, even at low temperature and without post deposition annealing. For $R_0 = 9$, the films have physical and chemical properties similar to those ob-tained by RF plasma enhanced chemical vapor deposition at 350°C, in terms of refractive index in the range of 1.47-1.48, etch rate in "P-etch" (6 Å/s), and Si-O-Si stretching mode vibration (1058 cm⁻¹). These films exhibit, at $R_0 = 9$ and 1200 W, electrical resistivity of $10^{15} \Omega$ cm and critical field larger than 3.5 MV cm⁻¹, without post-deposition annealing.

Dielectric layers can be used for a large number of applications in silicon, III-V, and II-VI compound semiconductor processing, (1) as: insulating layers in insulated gate field effect transistor (IGFET): thermal silicon dioxide has been accepted for a long time as the ideal gate insulator on silicon substrate due to the low interface state density achieved at the SiO₂-Si interface. This problem is not resolved for III-V compounds; insulating layers between metallization lines of integrated circuits: they are currently made with silicon dioxide. High conformal step coverage is needed because of the complicated surface geometries; passivation and capping layers: silicon nitride has several advantages compared to silicon dioxide such as higher density, better impurities diffusion mask, lower pinholes density (2)...

Plasma enhanced chemical vapor deposition using radio frequency (13.56 MHz) excitation (RF PECVD) is the most commonly used technique for dielectric deposition. In this system, the discharge is created between two parallel-plate electrodes in a mixture of SiH₄ and N₂O and the substrates are located in the discharge. Despite long research, the quality of silicon dioxide deposited by RF PECVD at low substrate temperature ($T_s < 150^{\circ}$ C) has been far from that of thermal oxide. It is commonly observed that RF PECVD oxide films present contaminations with Si-H,

¹Present address: Thomson-CSF LCR, Domaine de Corbeville, 91404 Orsav Cedex France.

Electrochemical Society Active Member.

N-H, O-H, Si-N bonds depending on the gases used (3). These bonds can passivate or create traps in the silicon dioxide films (4). For many PECVD processes, increasing the substrate temperature decreases the hydrogen contamination (5,6) and improves bulk electrical properties. At a substrate temperature of 350°C, silicon dioxide PECVD films typically contain 10 a/o of hydrogen (6).

The aim of the recent investigations in the field of PECVD (2, 4, 6) is to improve the quality of the deposited films at a lower deposition temperature. It was reported recently that high quality silicon dioxide can be obtained by RF PECVD using low flow rates of reactive gases (SiH₄ and N₂O) diluted in a large flow rate of He, at substrate temperature of 350°C (2). According to Batey et al., the dilution in He improves the uniformity and the reproducibility. Electrical quality of these films deposited on Si, shown through resistivity ($\rho > 5 \times 10^{15}\Omega$ cm) and interface state density measurements ($N_{ss} = 4 \times 10^{10}$ cm⁻² eV⁻¹), is not far from that of a conventional thermal oxide. Here, it becomes possible to use PECVD films for IGFET applications.

In order to decrease the high hydrogen contamination of the RF PECVD films, Lucovsky developed a system in which SiH₄ is injected outside the discharge near the substrate. This system is called remote plasma CVD (4). Large flows of oxidant gases diluted in He sustain the discharge and the stream of excited oxygenated species react with SiH₄ at the substrate surface. This configuration decreases

Downloaded on 2015-03-19 to IP 128.255.6.125 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms use) unless CC License in place (see abstract).

gas phase reactions due to SiH₄ at a mbar range plasma pressure. Gas phase products could be at the origin of unwanted bonds in the films, Si-O-H or H₂O (4). According to Lucovsky *et al.*, the use of the He-SiH₄ chemistry enhances hydrogen elimination. At a substrate temperature of 350°C, the hydrogen content is below the detection level of infrared spectroscopy (IRS), which is around 1 atomic percent (a/o) on 1 µm thick films.

In conclusion, with RF plasma excitation, whatever is the configuration (remote or not, with or without helium dilution) the substrate temperature has to be larger than 250°C to obtain good electrical quality SiO₂ films ($\rho > 5 \times 10^{15} \Omega$ cm). This temperature can be too high for III-V and II-VI compound applications, and it is crucial to reduce the temperature as low as possible. Moreover, lower deposition temperature could be of interest for modern silicon based ultra large scale integration (ULSI) technology (7).

At this time, only microwave PECVD allows low temperature deposition of high quality dielectric thin films (6, 8, 11). This is due to the high reactivity of microwave plasma at electron cyclotron resonance (ECR) conditions. High densities of low-energy ions enhance surface reactions without substrate heating. Dense films can be obtained at a high deposition rate (8). Note that, according to Herak, the deposition temperature of ECR PECVD oxide has to be larger than 300°C to obtain high electrical quality films (9).

The deposition of high electrical quality films at low temperature remains an open challenge. In this paper, we present and discuss the silicon dioxide deposition process at low temperature ($T_{\rm s} < 120^{\circ}$ C) by distributed electron cyclotron resonance (DECR) microwave PECVD (10-13). In this work we studied the effect of the gas mixture on the bulk physicochemical and electrical properties of SiO₂ thin films. The study of SiO₂-semiconductor interface properties is reported elsewhere (14). In order to evaluate the effects of microwave power, the experiments were performed at two different power values.

Description of DECR Plasma

Deposition apparatus.—The experiments were performed in a multipolar microwave (2.45 GHz) plasma reactor provided by ALCATEL (RCE160), which uses DECR configuration. The reactor is composed of two separate chambers, one for loading and one for deposition; both are evacuated by turbomolecular pumps to residual pressures below 2×10^{-7} mbar. Pure SiH₄ and N₂O (electronic grade) are introduced in the chamber through mass-flow controllers (range 0-20 sccm). During deposition, pressure is regulated by a throttle valve and compared with baratron gauge indicator. The substrate holder can be heated up to 400°C or cooled with flowing water; it can also be RF (13.56 MHz) biased.

DECR concept.-The DECR excitation associates microwave antennas and multipolar magnetic field produced by a set of permanent magnets. It creates local ECR zones distributed around the chamber, confines plasma at low pressures, and traps energetic electrons. The permanent magnets are fixed outside the chamber along its vertical direction. They present alternate polarity to the plasma so that the magnetic field lines are included in the horizontal section of the reactor which is also the substrate plane. As a consequence, the defects caused by charged particles drifting along the magnetic field lines should be lower as compared to a classical ECR configuration where magnetic field lines are perpendicular to the substrate plane. The decrease of the magnetic field induced by a set of permanent magnets in a multipolar configuration is faster than the decrease of the coil induced field. As a consequence, substrates are located in a quasi-magnetic free region (B < 10 Gauss). Microwave power is coupled to the plasma by the use of waveguide, distributor, coaxial cables, feedthroughs, and applicators.

The use of eight linear microwave applicators, an applicator per magnet, creates sixteen ECR zones distributed along the magnets and all around the chamber, as shown in Fig. 1. Eight applicators are required for 4 in. substrates and fourteen applicators for 8 in. substrates. Energetic



Fig. 1. Schematic top view of a DECR reactor, showing the different plasma regions.

electrons created in the ECR zones (the cusps) are trapped in the magnetic lobes between two magnets. The high energy particles are reflected by the magnetic mirror to the periphery of the reactor and the low energy particles diffuse into the center of the chamber where the substrate is located. This is why DECR process can be considered as a more gentle process than the RF process. The electronic density and ionic current density are much larger than in RF plasmas but the plasma potential and the electronic temperature are lower (12-13).

Plasma characterizations.—Figure 2 presents ionic current densities measured in the reactor, as a function of the pressure, for a pure Ar plasma, at different microwave power values. Current is collected by the substrate holder biased at $-20 V_{dc}$. This voltage is sufficient to obtain ionic current saturation. high current density values are ob-



Fig. 2. Effect of gas pressure on ionic current densities collected in Ar plasmas, by the substrate holder biased at $-20 V_{dc}$, for Ar plasmas, at different microwave power.

tained for pressure between 0.5 and 1.5 µbar. At lower pressure, current is limited by the density of neutral species. At higher pressures, the efficiency of DECR configuration decreases, due to the decrease of mean free path. Using the electronic temperature value measured by Pichot ($T_e = 3 \text{ eV}$, Ref. 12), one can estimate with the ionic current value that ionic density is $8 \times 10 \text{ cm}^{-3}$ at 800 W.

Experimental Procedure

Sample preparations.—Deposition was done on Si substrates and simultaneously on GaAs substrates. Substrates were degreased before each run by standard procedure including trichlorethylene, acetone, and propanol successive baths. Si was deoxidized in HF/H_2O (1:1) and rinsed in flowing DI water, whereas GaAs was deoxidized in pure HCl and rinsed in propanol. *In situ* cleanings were not performed. Thickness of the films is close to 100 nm, as typically used in IGFET devices.

Film characterizations.—Film refractive index and thickness were determined using a Rudolph Research null ellipsometer at a wavelength of 5461 Å and MacCrackin calculation programs, assuming nonabsorbent films.

MeV ion beam analysis techniques (IBA) were used to determine atomic composition of the films. Oxygen, nitrogen, and silicon contents were measured using characteristic nuclear reaction analysis (NRA), (15-16) and hydrogen content using elastic recoil detection and analysis (ERDA). As already explained (17), measurements were performed on films deposited on GaAs substrates, especially for Si content determinations. These techniques enable the determination of the absolute value of the number of specified atoms per square centimeter in the films. Volume densities (at cm⁻³) can then be obtained by combining IBA (at cm⁻²) and ellipsometry results. Errors in the concentration values lie below 5% for Si and N, 3% for O, and 10% for H.

Chemicals bonds in the films were studied by Fourier transform infrared spectroscopy (FTIRS) (Perkin-Elmer FT1700, transmission mode) between 4000 and 450 cm⁻¹. Films were deposited on double-sided polished undoped silicon substrates and substrate absorbance was used as the background during analysis. FTIRS is a useful tech-



Fig. 3. Hydrogen yield in ERDA measurements on SiO₂ films as a function of the accumulated dose of the 2 MeV ⁴He analysis beam. The films were obtained at 800 W, $R_o = 2$ (\bullet) and $R_o = 9$ (o). The inset shows the schematic principles of ERDA measurements.

nique to study local atomic structure of silicon dioxide thin films and to demonstrate the presence in the films of unwanted bonds like SiOH, SiH, or H_2O .

The global physical behavior of the films was studied by measuring the etch rate in a "P-etch" solution, HF(40%):HNO₃(65\%):H₂O, of 3:2:60 (18). The film etch rate was simultaneously compared to the one of a thermal silicon dioxide. The etch rate is very sensitive to chemical bonds and porosity and reveals inhomogeneities in the films.

We utilize quasistatic-ramp current voltage characteristics to measure electrical properties of the films. Measurements are performed on Al-SiO₂-Si diodes. The surface of the thermal-evaporated aluminum dots is 2.8 10^{-3} cm². As first described by DiMaria (19), this technique leads to accurate measurements of bulk insulating properties because of the low voltage sweep rate (0.1 V/s) and high voltages scanned (0-100V). Current induced in the MIS diode would be purely capacitive ($C_i dV/dt$) for an ideal insulator ($\rho > 10^{16} \Omega \cdot$ cm). In reality, the current observed presents two different regimes. In the first regime, the current is constant ($\rho > 10^{16} \Omega$ cm) or increases linearly with the applied voltage ($\rho = 10^{14} \cdot 10^{16} \Omega$ cm). In the second regime, the current increases rapidly when large injection current occurs from the electrode (2, 19).

We call critical field (E_c) the electrical field which leads to injection current density of 10^{-9} A cm⁻² (20). This value is small, compared to capacitive current, approximately 5×10^{-9} A cm⁻² for our samples. Batey calls this regime "premature injection" (2). For some of our samples, I(V) characteristics exhibit linear slope at low electric field. This is due to resistivity in the range 10^{14} - 10^{15} Ω cm. For these samples, E_c is determined as explained in the inset of Fig. 8.

Analysis of Hydrogen Content

The measurements of the hydrogen density in the layers were performed using ERDA (21). In this technique, the sample is bombarded with mono energetic MeV ⁴He ions. The target hydrogen atoms recoiling forward under elastic collisions with incident particles, are detected and counted.

For surface analysis of thick samples, the directions of incident beam and detected particles cannot be far from the surface plane. In order to get rid of the numerous scattered particles and of the other atoms recoiling from the samples, an absorber foil is placed in front of the detector. The thickness of this absorber is chosen to stop all the particles coming from the target except hydrogen atoms, taking advantage of the fact that the stopping power for hydrogen is much less than for the other atoms or ions. The inset in Fig. 3 illustrates the above schematic description.

In our experiments, we used a 2.2 MeV ⁴He beam produced by the 2.5 MeV Van de Graaf at the Groupe de Physique des Solides. The detection angle was $\theta_{iab} = 30^{\circ}$, the sample normal being 75° from the incident beam direction. The normal to the surface sample, the beam, and the detection direction are all in the same horizontal plane. The absorber used as a 10 μ m thick aluminized Mylar foil. The detector used is a standard 3 cm² surface barrier semiconductor detector; a diaphragm with a verticle 1 × 18 mm² aperture was placed in front of it so determining precisely the detection angle; the detection solid angle was 2.378 mstrad.

As the hydrogenated layers are thin enough (\approx 100 nm), the energy spectrum of the recoiled hydrogen atoms has a peak shape (full width at half maximum, FWHM \approx 100 ke V). This allows an easy integration of the total corresponding counts.

The absolute values of the hydrogen content were determined using the cross-sectional values measured by Szilagyi *et al.* (22). A usual problem in such measurements is the hydrogen loss in the sample due to damage produced by the analyzing beam. To overcome this difficulty and reach the original value of hydrogen content, we registered systematically the hydrogen counts as a function of the total dose of incident particles. The value of hydrogen content was then determined by extrapolation to zero dose (Fig. 3). Residual pressure in the analysis chamber was maintained below 10⁻⁶ mbar. A liquid nitrogen cooled trap was used to keep the "C-H" residual pressure as low as possible. A correction for initial hydrogenated surface pollution, measured with a clean Si substrate, was applied. It was always below 5×10^{15} cm⁻². As the typical value of hydrogen content in the analyzed film was always found to be larger than 5×10^{16} cm⁻², the above corrections represent less than 10%.

Results and Discussions

Deposition procedure.—All experiments described in this paper have been performed without intentional heating. Studies performed at CNET Meylan (France) on DECR Ar plasma showed that the surface temperature of a silicon substrate exposed to the plasma during 20 min at floating potential rises only to 80° C (23). We have checked the temperature under our deposition conditions, using thermosensitive paints and thermocouples, and we confirm that the substrate temperature stays below 120°C during deposition.

Total pressure is fixed at 1 µbar which is the typical working pressure in DECR plasma. Total gas flow is fixed at 20 sccm, while ratio of SiH₄ to N₂O flow rate is varied. When maximum pumping speed is used (350 l/s), pressure equal to 0.6 µbar is obtained. Pumping speed is thus constant for all deposition runs.

Experiments were performed for two different microwave power values, 800 and 1200 W. Due to the threedimensional geometry of the DECR plasma, it is quite difficult to define the power density injected in the plasma; however, taking into account that the plasma surface seen by the sample is around 2000 cm², densities of 0.4 and 0.6 W cm⁻² can be suggested. The matching of the microwave generator to the plasma did not have to be changed when changing operating conditions, gas, pressure, or power.

The ratio of N₂O flow to SiH₄ flow (R_o) was varied from 1 to 9, while keeping total gas flow constant. This range of R_o values is limited by mass-flow controller characteristics.

The fact that the DECR plasma is very efficient in dissociating SiH₄ molecules can be illustrated by the following experiment. The pressure obtained in the reactor with a 10 sccm flow of SiH₄ is 0.4 µbar. If one switches on the plasma, the pressure increases to 1.5 µbar. This means that SiH₄ is greatly dissociated in DECR plasma certainly with high hydrogen production.

Ellipsometric results.—The variation of deposition rate (d_r) and refractive index (n) of the films deposited on silicon substrates as a function of the ratio R_o are reported on the Fig. 4. The deposition rates are mean values, corresponding to a total number of runs exceeding 100 and the standard deviation is quoted as the uncertainty. The uniformity of the films deposited on a 2 in. silicon substrate was measured for two different gas phase compositions: $R_o = 5.7$ and 9. The thickness of the films was found to be uniform within $\pm 1\%$, and no significant variation (< 0.005) was observed on refractive index. The same uniformity is achieved for all deposition conditions. It was observed that the deposition rate and refractive index exhibit similar values and variations on GaAs and InP substrates.

We observe two different regimes with SiH₄ dilution: between $R_0 = 1$ and 4, deposition rate decreases from 25 nm min⁻¹ to 14 nm min⁻¹ and refractive index decreases from 1.7 to 1.5. These values, larger than that of the high temperature silicon dioxide one, indicate nonideal SiO₂ films. Because the refractive index depends on stoichiometry, density, and contamination, more analyses are needed to explain these large values. For $R_0 > 4$, the deposition rate further decreases with SiH₄ dilution and it is equal to 6.5 nm min⁻¹ for $R_0 = 9$. Note that refractive index for $R_0 > 4$ is close to 1.475 ± 0.005 for all different gas phase compositions and for a large number of deposition runs. This value would correspond to a thermal oxide grown at less than 800°C (24).

Plotting the deposition rate as a function of SiH₄ flow, we found a linear dependence from 2-7 sccm, even for different total gas flow (*i.e.* different pumping speed). This in-



Fig. 4. Deposition rate and refractive index vs. gas flow ratio (800 W, 1 $\mu bar).$

dicates the presence of a mass-transfer controlled deposition reaction as recently described by Shirai (25) for very low-pressure plasmas. Similar conclusions were reported by Cooke for this system (10).

Similar results (refractive index and deposition rate) are found for microwave power value of 1200 W and $R_0 > 4$.

Film stoichiometry.—Atomic densities of Si, O, N, and H in the films as a function of the gas phase composition are reported on the Fig. 5. These densities in at cm^{-3} are deduced from NRA and ellipsometry measurements. Measurements are typically performed on GaAs samples but results are equivalent on Si and InP, in terms of O, N and H contents.

As already observed on refractive index, two different regions are evident. When $R_o > 4$, the films are mostly composed of silicon and oxygen atoms with less than 5×10^{21} H cm⁻³ and less than 2×10^{21} N cm⁻³. We can notice that these physical characteristics (*i.e.* refractive index, deposition rate, and atomic composition) are independent of the microwave power (800 or 1200 W) in the high SiH₄ dilution regime ($R_o > 4$). For $R_o < 4$, larger refractive indexes observed can be explained by the presence of high nitrogen density. When $R_o = 1$, the stoichiometry is approximately that of SiONH. As shown in Fig. 3, the beam-induced loss of hydrogen in the films much depends on the global stoichiometry of the films, suggesting different bonding of H in the films.

As all atomic densities are known, contaminations can be expressed in a/o, *i.e.* (H or N)/(Si + O + N+ H) (Fig. 5). The contaminations decrease as the ratio R_o increases. It means that hydrogen incorporation decreases as SiH₄ flow decreases but that nitrogen incorporation decreases at N₂O flow increases. This confirms that plasma oxidation of silicon is easier than plasma nitridization. For $R_o > 5$, nitrogen and hydrogen contaminations are reduced to about 2 and 5 a/o and all atomic concentrations are quite constant. Decrease of contaminations in the films as R_o is increased could be due to a change in the plasma chemistry, induced by the SiH₄ dilution in N₂O.

In the high SiH₄ dilution regime, silicon and oxygen concentrations are close to thos observed in the high temperature material: $N_{\rm si}$ (thermal SiO₂) = 2.2 × 10²² cm⁻³, $N_{\rm o}$ (ther-



Fig. 5. Atomic densities of Si (\Box), O (\bullet), N (o), and H (Δ) atoms vs. gas flow ratio (800 W, 1 µbar). The dotted line indicates the oxygen density in thermal silicon dioxide.

mal SiO₂) = 4.4×10^{22} cm⁻³. Our results suggests that these films are slightly oxygen rich. The excess of oxygen could be due to the presence of Si-O-H or Si-O-N- bonds.

Preliminary results obtained using Rutherford back scattering (RBS) did not show metallic contaminations, owing to the sensitivity of the technique for 1000 Å films $(10^{13} \text{ cm}^{-2})$.

Atomic bonds in the films.—We have examined the nature of the bonding groups by infrared spectroscopy (IRS) measurements. IR absorption spectra exhibit three principal bands associated with the Si-O-Si stretching mode (near 1075 cm⁻¹), bending mode (near 800 cm⁻¹, and rocking mode (near 465 cm⁻¹). The frequency associated with the stretching mode (v) is usually used, in order to follow structural modifications of the Si-O-Si bond, rather than the bending and rocking mode frequency. The value of this frequency depends on the angle of the Si-O-Si bond (145° for thermal oxide). In the same time, the FWHM value (Δv) increases as the distribution of bond angles broadens. As discussed recently by Fitch *et al.* (26), the values of vand Δv are connected. This was observed for different oxides, thermal or deposited, with or without high temperature post-annealing. The values of v as a function of R_o are reported on the Fig. 6. The value of v increases as R_o increases and saturates above $R_o = 4$, at a value of 1058 ± 2 cm⁻¹. As already observed by ellipsometry, the structure of our films should be different from that of the thermal oxide as v is smaller than the value observed in thermal oxide, 1075 cm⁻¹. At the same time, the FWHM value is larger (90 cm⁻¹) than that of thermal oxide (75 cm⁻¹). This observation is currently reported for nonthermal oxides. Our films deposited at low temperature are comparable, from this point of view, to RF PECVD films deposited at 350°C (6). Our results are in good agreement with the analysis of $\Delta v = F(v)$, published by Fitch *et al.* (26).

Unwanted bonds, most of the time H-related, can be observed as SiOH (3300-3600 cm⁻¹) SiH (2300 cm⁻¹) or H₂O (3000-3500 cm⁻¹) in SiO₂ thin films. Following literature, IRS detection level is about 0.5-1 a/o for relatively thick films (> 5000 Å). According to Herak, observation of 5% of SiOH in 1000 Å films can be performed (9). The detection of H-related bonds in our films obtained with high SiH₄ di-



Fig. 6. Si-O-Si stretching frequency vs. gas flow ratio (800 W, $1\mu\text{bar}).$

lution ($R_o > 4$) was not achieved in our experiments due to the low hydrogen content (5×10^{16} H cm⁻²). Films deposited with R_o between 1 and 3 exhibit mostly N-H and Si-H bonds with evident absorption bands.

The results reported above are independent of the microwave power value, for $R_0 > 4$.

Etching rate.—The oxides deposited by various CVD techniques can significantly differ in their resistance to "P-etch" dissolution. This solution was first used by Pliskin for the study of silicon dioxide-silicon interface (18). The values of etch rates obtained with different films, depending on method and temperature growth, are reported in the Table I. For near-stoichiometric films, low values of etch rates are commonly associated with high density and low contaminated oxides.

The etching rate was determined by ellipsometry by measuring the thickness of the oxide as a function of the etching time. The thickness was found to be a linear function of etching time and etch rate was deduced from four point plots. The etch rate of a thermal oxide (2Å/s) was simultaneously determined. For some deposition conditions (see below), the refractive index decreases with etch time. This was explained by the presence of an oxide surface roughness, induced by the etch, which indicates an inhomogeneous oxide microstructure.

Table I. "P-etch" rates and critical field of silicon dioxide films grown or deposited by different techniques. Film properties are compared although elaboration conditions are different (gas mixture . . .).

Method	Deposition temperature (°C)	Etch rate (Å s ⁻¹)	$E_{\rm c} ({\rm MV/cm})$ $I = 1 {\rm nA/cm^2}$	Ref.
Thermal	1150	2	5-6ª	(2)
RF PECVD ECR PECVD	$350 \\ 25$	8	5-6 1	(2) (9)
DECR PECVD	350 25	7 6	5 3.5	This work

^a These measurements were also performed with our experimental setup on samples obtained with the standard thermal process. The etch rates as a function of R_o , for power values of 800 and 1200 W, are presented on Fig. 7. The study was limited to the near-stoichiometric oxide films ($4 < R_o < 9$). The etch rate of the DECR oxides decreases when R_o increases and it is lower for films deposited at 1200 than at 800 W, in opposite to the other physical properties such as the refractive index, atomic composition and infrared absorption which values saturates for $R_o > 4$, whatever is the power. This observation suggests that "P-etch" is more sensitive to the global quality of the films and gives additional information. The lowest value obtained for $R_o = 9$ and 1200 W is 6 Å s⁻¹.

Furthermore, etch studies have shown that all films deposited at 800 W exhibit a decrease of refractive index during the dissolution, large for $R_0 = 4$ and weak for $R_0 = 9$. It should be emphasized that the refractive index of the films deposited at $R_0 = 9$ and 1200 W remain constant, indicating high homogeneous microstructure. These conclusions are further confirmed by electrical properties.

Bulk electrical properties.—Electrical properties were studied on 100 nm thick films, deposited at 800 and 1200 W, in relation with oxidant ratio in the gas phase. Whatever the microwave power value is, films deposited at low oxidant ratio ($R_o < 4$) exhibit poor electrical properties. Therefore, we only focus our attention on films deposited at high oxidant ratio ($R_o > 4$), which are nearly stoichiometric as previously discussed.

The variation of critical field values with oxidant ratio are reported in Fig. 8. These measurements are performed on silicon substrates (n-type, 0.01-1 Ω cm) without postdeposition annealing.

Critical field (E_c) increases as oxidant ratio increases and/or as microwave power value increases. Microwave power of 800 W leads to films which present the same physicochemistry as film deposited at 1200 W but with lower E_c values. At the same time, resistivity increases to reach 10¹⁵ Ω cm for $R_o = 9$. In this case, quasistatic I-V technique clearly demonstrates the two different leakage current mechanisms: linear at electrical field lower than E_c and nonlinear at electrical field higher than E_c . The best value of critical field achieved, for $R_o = 9$ and 1200 W, is 3.5 MV/cm. This value is slightly smaller than those obtained



Fig. 7. Etch rate of DECR oxides in "P-etch" solution, vs. gas flow ratio, at different microwave power (800 and 1200 W, 1 $\mu bar).$



Fig. 8. Critical field vs. gas flow ratio, at different microwave power values (800 and 1200 W, 1 μ bar). The inset shows a typical quasistatic I(V) characteristic, with ρ and E_c determination.

by other techniques, using higher deposition temperature (see Table I). It must be noted that our experimental conditions (power density, gas phase composition . . .) were not optimized in order to obtain the best SiO_2 film.

It is clear that critical field is not governed only by stoichiometry, since variations of critical field along the "stoichiometric" regime are observed in the range $R_0 = 4-9$.

Conclusions

In order to succeed with low temperature high quality dielectric deposition, we have used a promising new system, based on the DECR excitation of a SiH₄/N₂O mixture. In this work, we have studied the effect of gas phase composition on the physicochemical and electrical properties of silicon dioxide thin films deposited at low temperature ($T_{\rm s} < 120^{\circ}$ C) and at two different microwave power values (800 and 1200 W). It was found that atomic composition of the deposited films strongly depends on the gas phase composition (N₂O flow/SiH₄ flow) as, already reported, with radio frequency excitation (RF PECVD).

Combining the use of ion beam analysis, ellipsometry, infrared absorption, etch rate, and electrical property measurements, we were able to correlate the behavior of, on one hand, refractive index and infrared absorption with atomic composition, and, on other hand, of etch rate with electrical properties (critical field, resistivity). In the best conditions, the near stoichiometric films obtained in this study have similar electrical properties to those obtained by conventional deposition techniques, at significantly higher substrate temperatures ($T > 250^{\circ}$ C).

This work suggests that optimization of others parameters, such as microwave power or gas phase composition, or maybe substrate bias, can further improve the qualities of the low temperature deposited films.

Finally, the DECR microwave excitation is found to be very useful to produce dense thin films exhibiting good physicochemical and insulating properties without substrate heating. This is promising for the III-V compound applications.

Downloaded on 2015-03-19 to IP 128.255.6.125 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

Acknowledgment

This work was supported by CNRS (GDR86) and by Thomson CSF (Thomson Recherche).

Manuscript submitted July 25, 1992; revised manuscript received Jan. 13, 1992.

Universite Paris Sud (XI) assisted in meeting the publication costs of this article.

REFERENCES

- 1. S. M. Sze, "VLSI Technology," McGraw-Hill, New York.
- 2. J. Batey and E. Tierney, J. Appl. Phys., 60, 3136 (1986).
- A. C. Adams, Solid-State Technol., 26, 135 (1983).
 G. Lucovsky, P. D. Richard, D. V. Tsu, S. Y. Lin, and R. J. Markunas, J. Vac. Sci. Technol., A4, 681 (1986).
- 5. A. C. Adams, F. B. Alexander, C. D. Capio, and T. E. Smith, *This Journal*, **128**, 1492 (1981).
- S. V. Nguyen and K. Albaught, *ibid.*, **136**, 2835 (1989).
 N. Raley, R. Hsu, C. Y. Fu, and D. Storms, Abstract 179, p. 270, The Electrochemical Society Extended Abstracts, Vol. 90-1, Montreal, Quebec, May 6-11, 1000 1990.
- 8. S. Matsuo and M. Kiuchi, Jpn. J. Appl. Phys., 22, L210
- (1983). 9. T. V. Herak and D. J. Thomson, J. Appl. Phys., **67**, 6347 (1990).
- 10. M. J. Cooke and N. Sharrock, in "Plasma Processing," G.S. Mathad and D.W. Hess, Editors, PV 90-14, p. 538, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1990).

- 11. F. Plais, B. Agius, F. Abel, J. Siejka, M. Puech, and P. Alnot, *ibid.*, p. 544; F. Plais, B. Agius, F. Abel, J. Siejka, M. Puech, P. Alnot, and N. Proust, Abstract 317, p. 460, The Electrochemical Society Extended Abstracts, Vol. 90-2, Seattle, WA, Oct. 14-19, 1990.
- 12. M. Pichot, A. Durandet, J. Pelletier, Y. Arnal, and L. Vallier, Rev. Sci. Instrum., 59, 1072 (1988).
- 13. R. Burke and C. Pomot, Solid-State Technol., 31, 67 (1988).
- 14. F. Plais, B. Agius, N. Proust, S. Cassette, G. Ravel, and M. Puech, Appl. Phys. Lett., 59, 12 (1991). 15. G. Amsel, J. P. Nadai, E. D. Artemare, D. Daiv, E. Gir-
- ard, and J. Moulin, Nucl. Instr. and Methods., 92, 481 (1971)
- 16. I. C. Vickridge, ibid, B34, 470 (1988).
- T. Carriere, B. Agius, I. Vickridge, J. Siejka, and P. Alnot, *This Journal*, **137**, 1582 (1990).
 W. A. Pliskin and R. P. Gnall, *ibid.*, **111**, 872 (1964).
- 19. D. J. DiMaria, R. Ghez, and D. W. Wong, J. Appl. Phys., 51, 4830 (1980).
- N. Proust, F. Plais, and B. Agius, Solid-State Electron-ics, 33, 227 (1990).
- 21. J. L. Ecuyer, C. Brassard, C. Cardinal, J. Chabbal, L. Deschenes, J. P. Labrie, B. Terreault, J. G. Martel, and R. St. James, J. Appl. Phys., 47, 381 (1976).
- 22. E. Szilagyi, F. Paszti, A. Mannuaba, C. Hadju, and E.
- Kotai, Phys. Rev. B 43, 502 (1989).
 X. Guillermet, Thesis, Grenoble (1989).
 J. T. Fitch, S. S. Kim, C. H. Bjorkman, and G. Lucovsky, J. Electron, Mat., 19, 151 (1990).
 K. Guillermet, C. G. L. J. Kim, C. 19, 151 (1990).
- K. Shirai and S. Gonda, J. Appl. Phys., 67, 6281 (1990).
 J. T. Fitch, G. Lucovsky, E. Kobeda, and E. A. Irene, J. Vac. Sci. Technol., B7, 153 (1989).

Correlation Between DLTS and TRXFA Measurements of Copper and Iron Contaminations in FZ and CZ Silicon Wafers; **Application to Gettering Efficiencies**

B. Hackl and K.-J. Range

Universitat Regensburg, Institut für Anorganic Chemie Universitatsstr. 31, W-8400 Regensburg, Germany

P. Stallhofer and L. Fabry

Wacker Chemitronic GmbH, P.O. Box 1140, W-8263 Burghausen, Germany

ABSTRACT

Metals forming deep traps in Si such as Fe, Cu, and Ni, are detectable with deep level transient spectroscopy (DLTS). In the present work, we used a spin-on technique as contamination method, which guaranteed sets of silicon wafers with authentic samples of iron- and, respectively, copper-contamination, that showed impurity concentrations on the wafer surfaces in the range of 10¹¹ and 10¹³ atoms/cm². A correlation between total reflection x-ray fluorescence analysis and DLTS has also been successful. Monitoring the iron content by DLTS in the course of gettering processes, we determined external and internal gettering efficiencies. Our compelling results showed a limited gettering efficiency at the oxygen precipitate sites, due to the level of iron contamination.

Metals, especially iron, copper, and nickel cause performance failures of devices and drastically reduce the manufacturing yield. Their detrimental impact on leakage current, gate oxide quality, and defect generation has thoroughly been investigated (1). Studying of the properties of the transition metals in semiconductors like the gettering behavior and, in conjunction with it, the ongoing search for analytical methods with improved detection limits for metal contaminations down to the ppt-range, are pertinent subjects in the field of the semiconductor silicon technology. Thus, the control of metallic contamination of silicon wafers in the ultra large scale integration (ULSI) technology is a challenge for the analytics, and only few techniques are presently applicable.

Two of the most suitable techniques are the deep level transient spectroscopy (DLTS) (2, 3) as a bulk specific analytical method with detection limits even below 5×10^{10} atoms/cm³ (depending on the dopant concentration) and the total reflection x-ray fluorescence analysis (TRXFA) (4) as a surface specific analytical method of high sensitivity $(10^{10} \text{ atoms/cm}^2).$

After driving the surface contaminant into the Si-bulk at higher temperatures (2), DLTS can also be applied for surface analysis. The DLTS method was also used to determine gettering efficiencies after external and internal gettering processes.

Authentic samples of contaminated silicon wafers were prepared, using the "spin dryer technique" (5).

Contamination Technique and Chemical Mechanism In 1988 M. Hourai described a method for quantitative contamination of hydrophilic silicon wafer surfaces with