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Low-temperature oxidation of silicon in microwave oxygen plasma

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The growth of silicon dioxide at low temperature in an oxygen plasma is investigated using a simplified electrodeless microwave discharge arrangement. The growth behaviour of the oxide is discussed in terms of plasma parameters. The compositional and electrical characterization of the grown oxide have been made to examine its performance for device applications. The results are compared with earlier observations by other authors.

1. Introduction

The achievement of high-yield very large scale integrated (VLSI) circuit necessitates low-temperature film formation in many steps during integrated circuit (IC) fabrication. One of the key steps is the formation of silicon dioxide films either by native oxide growth or deposition from a gaseous source. The conventional high-temperature process of thermal oxidation or chemical vapour deposition gives rise to undesirable impurity redistribution and the formation of defects such as dislocations, stacking faults and "bird's beak". Low-temperature oxide formation is thus necessary to avoid the degradation of performance and yield of VLSI circuits. Plasma oxidation using highly activated oxygen species is one of the low-temperature alternatives to thermal oxidation.

The most widely investigated plasma technique is plasma anodization with a high growth rate. However plasma anodization using a positive d.c. potential applied to the silicon substrate has several disadvantages, such as contamination caused by electrode sputtering, or damage caused by irradiation of energetic charge particles. Plasma oxidation carried out in an electrodeless chamber has not received much attention due to the difficulty in achieving high oxidation rates. Studies have been carried out by several authors [1–5] to oxidize silicon in a d.c. and radio frequency (RF) plasma discharge of oxygen at temperatures below 600° C. The study by Ray and Reisman [2] in RF plasma discharge resulted in an oxide with a moderate growth rate, low defect densities and improved interfacial properties comparable to thermal oxide after a post-oxidation annealing cycle. Field effect transition (FET) devices made with plasma oxide [3] were found to be comparable to those made with thermal oxide. Studies are now continuing to grow good quality plasma oxides in different chamber configurations, different frequencies of the applied field and over a wide pressure range. Special attention has been claimed by techniques for growing oxides in microwave plasma utilizing some unique features of this plasma, namely

(i) a high degree of ionization resulting in rapid growth rate;
(ii) sustenance of plasma over a wide pressure range from as low as 10^{-5}Torr; and
(iii) development of low self bias at the substrate eliminating radiation damage due to ion bombardment.

The use of microwave oxygen plasma with high plasma densities was made in the mid-1960s [6, 7] to achieve a high growth rate of oxides at low temperature. The work of Ligenza [6] was aimed at a study of oxidation and its growth behaviour. Kraitchman [7] and Kimura *et al.* [8] studied the growth and properties of microwave plasma oxides in the absence and presence of magnetic field, but its interfacial properties were not reported. Roppel *et al.* [9] and Musil *et al.* [10] studied the interfacial properties of the microwave plasma oxide and reported a relatively high value of oxide charge density. The structural properties of their oxide were apparently not investigated. It would thus appear that there is a need for a detailed study on the growth and both physical and electrical properties of the oxides grown in a microwave plasma. Section 2 below deals with the experimental technique for the growth of silicon dioxide film at low temperature using a simplified microwave plasma discharge arrangement. An attempt has been made to explain the growth behaviour of the oxide, and its structural characterization using infrared spectroscopy, etch rate measurements and X-ray photoelectron spectroscopy (XPS) analysis. The interfacial and electrical properties of the oxide have been extracted from capacitance–voltage (C–V) characteristics of fabricated aluminium-gate metal-oxide-semiconductor (MOS) capacitors. An effort has been made to improve the oxide properties by a proper annealing cycle.

2. Experimental procedures

A schematic diagram of the microwave plasma oxidation system used in our work is shown in Fig. 1. The arrangement consists of a microwave cavity (37 × 37 × 26 cm^3) discharge system incorporating a magnetron of power 700 W at a frequency of 2.45 GHz. The power is transported to the cavity through a

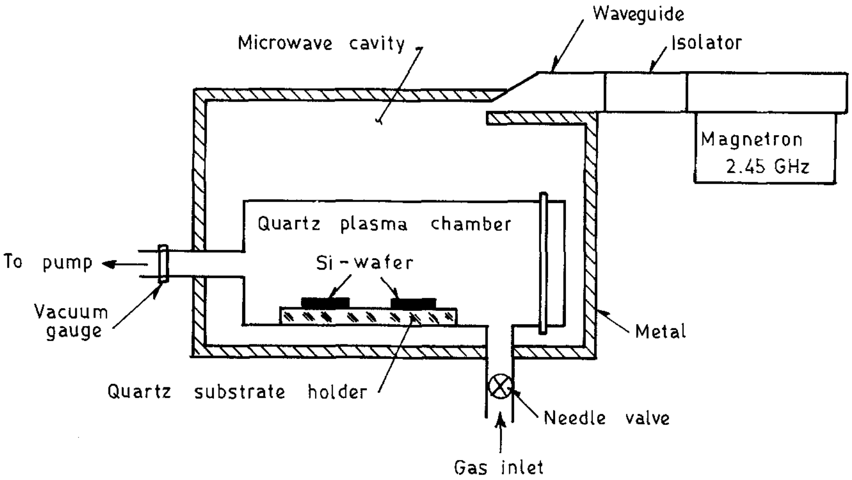

Figure 1 Schematic diagram of the microwave plasma oxidation system.

rectangular waveguide with built-in isolators. The quartz discharge chamber (5 cm i.d.) backed by a rotary pump (100 lit min^{-1}) was evacuated to 100 mtorr and was then flushed by a high purity oxygen flow at 2 torr for five min. The oxygen pressure controlled by a needle valve was then adjusted to the working range. The chamber filled with oxygen was placed in the cavity for the microwave energy to strike the plasma. The colour of the plasma appeared to be pale red or greenish depending upon the chamber pressure range and its placement in the microwave cavity. In the present work, the colour of the plasma was green at our working pressure regime of 400 to 500 mtorr. The volume of the plasma in the chamber varied with pressure; the plasma constricts into the centre region of the chamber at a pressure of 2 torr and above.

Silicon samples (2 × 2 cm) of both n-type (3 to 5 Ω cm) ⟨1 1 1⟩ and p-type (7 to 14 Ω cm) ⟨1 1 1⟩ were used for oxidation. The pre-oxidation cleaning of wafers was done successively in a mixture of sulphuric acid and hydrogen peroxide, deionized (DI) water, dilute hydrofluoric (HF) and DI water. No external d.c. bias was applied to the substrate, nor was an independent external heating of the substrate made in our experiment. The temperature of the discharge measured at the outer wall of the chamber was nearly 400° C. Even at this low substrate temperature a moderately high growth rate of oxide film, typically 210.0 nm in 7 min, has been observed.

3. Results and discussion

3.1. Growth behaviour

The growth behaviour of plasma oxide on an n-silicon sample for typical experimental conditions is shown in Fig. 2. The oxide thickness was measured by an ellipsometer. The growth behaviour is generally a mixture of linear and parabolic characteristics as in thermal oxidation, with major differences in temperature and thickness ranges. Similar growth behaviour was observed by Kimura *et al.* [8] in their magneto-active microwave plasma oxidation experiment. They explained the growth behaviour by the Deal–Grove thermal oxidation model, and calculated the linear and parabolic rate constants. The negative sign of the linear rate constant was explained by a modified Deal–Grove model in which oxygen ion migration was assumed. On the other hand, the results obtained by Ligenza [6], Kraitchman [7] and Roppel *et al.* [9] for isotropic microwave plasma were analysed by assuming the growth behaviour as essentially parabolic. The growth behaviour under the present experimental conditions can be explained by a parabolic equation, as shown in Fig. 2, with a rate constant value that is in agreement with the observations of Ligenza [6] and Kraitchman [7]. The rate constant values obtained in different studies are listed in Table I. The initial slow rate of oxidation for 30 sec in the present study may be due to the finite time taken for the creation of a stable discharge after switching on the microwave power and heating the sample to the gas temperature.

In the present experiment, oxide growth ceases (i) above a certain pressure (~500 mtorr) although oxygen plasma exists; and (ii) when the inlet–outlet of the reactor is interchanged. The phenomenon of no oxide growth above a limiting pressure may be due to the fall of electron density and/or the floating potential of the plasma with respect to the silicon sample. This is in agreement with the observation of Musil *et al.* [10] who also observed that oxide films are formed at a certain pressure interval when the floating potential of the plasma $U_{fl} \geqslant -10\,\text{V}$ corresponding

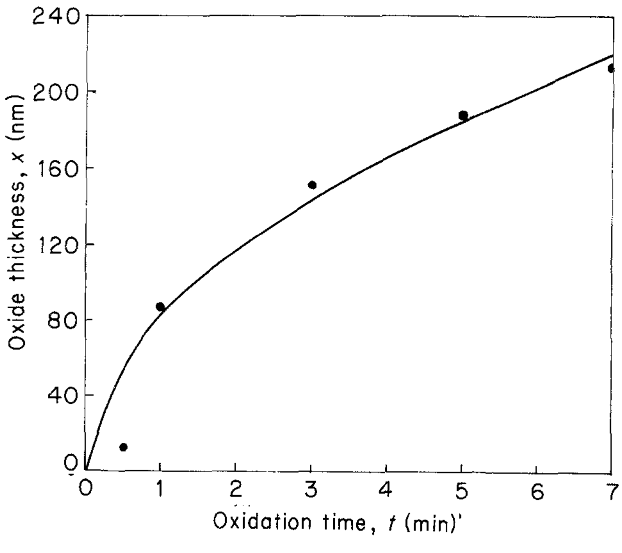

Figure 2 Oxide thickness as a function of time for microwave plasma oxidation microwave power, 700 W; oxygen pressure, 400 mtorr; sample, *n*-silicon, 3 to 5Ω-cm^{-1}, ⟨1 1 1⟩. $X^2 = Bt$; $B = 6.9 \times 10^5$. ●, Experimental points.

TABLE I Rate constant values in microwave plasma oxidation at different experimental conditions

References	Temperature (°C)	Pressure (torr)	Growth model	B ($\text{nm}^2\,\text{min}^{-1}$)	B/A ($\text{nm}\,\text{min}^{-1}$)	T (min)
Ligenza [6]	430	0.5	Parabolic	0.049×10^5	–	–
Kraitchman [7]	<700	0.15	Parabolic	0.0187×10^5	–	–
Kimura [8]	400	2.10^{-4}	Linear–Parabolic	0.0325×10^2	-0.373	1.05
Roppel [9]	300	0.3–0.15	Parabolic	$0.0042\text{–}0.081 \times 10^4$	–	–
This study	400	0.4	Parabolic	0.069×10^5		

Rate equation, $X^2/B + X/(B/A) = t + T$, where X is the oxide thickness at any time t, B is the parabolic rate constant, B/A the linear rate constant and T the time to grow initial oxide thickness.

to an electron density $Ne \geqslant 7 \times 10^{12}\,\text{cm}^{-3}$. However, oxidation in their experiment took place over a wide pressure range from 5×10^{-5} torr to 1 torr due to the generation of high plasma density, $> 10^{12}\,\text{cm}^{-3}$, in the presence of an external magnetic field under electron cyclotron resonance (ECR) condition. The effect on oxide growth of interchanging the inlet–outlet of the reactor also follows the observation of Loncar *et al.* [11], who found that oxidation rate was a strong function of the location of the gas inlet into the chamber. This unknown factor, which plays an important role in the oxidation process, demands a detailed investigation of the growth mechanism. The growth does not show any profound effect of the type of sample, whether n or p, in our experiment. This result supports the plasma oxidation theory, which assumes that oxide growth is characterized by the dominance of ion and electron drift in the oxide, the supply of ions being limited by the density of the plasma, and is not therefore limited by surface reaction like thermal oxidation. The strong temperature dependence of oxide growth observed by Kimura *et al.* [8] also suggests a diffusion limited mechanism of microwave plasma oxidation. The diffusion is enhanced by the potential across the oxide originating from the floating potential around the specimen.

3.2. Structural and electrical characterization

To become a key process in VLSI fabrication, the quality of the plasma-grown oxide should be comparable to that of conventional thermal oxidation. But so far fabricated devices using plasma oxides in general show poor performances, as the oxide properties are significantly different from those of thermal oxides. To evaluate the performances of plasma-grown oxides structural and electrical characterization has been carried out.

The refractive index of the oxide is measured with an ellipsometer (Gartner L117) incorporating laser light of wavelength 632.8 nm. A variation of the refractive index values from 1.45 to 1.47 is observed in the grown oxides. The physical and structural properties of the grown oxides were characterized by IR absorption spectra, etch rate measurements and X-ray photoelectron spectroscopy (XPS) analysis. The infrared absorption spectra of the grown oxides were evaluated to provide information about the local bonding environments of the constituent atoms of the oxide films. The measurements have been made with an IR spectrophotometer (Perkin-Elmer 598) in the wave-number scanning range from 200 to $4000\,\text{cm}^{-1}$. Figure 3 shows the IR transmission spectra of plasma-grown silicon oxide samples together with the spectra of thermally grown oxides. Some small peaks observed below $600\,\text{cm}^{-1}$ and above $2500\,\text{cm}^{-1}$ are ignored in the analysis. The dominant feature of IR absorption spectra of both thermal and plasma grown oxide is associated with the stretching motion of oxygen atoms. It is known [12] that the frequency of the stretching band scales monotonically with the composition in SiO_x alloys ($x < 2$), from about $940\,\text{cm}^{-1}$ for oxygen-doped amorphous silicon to about $1075\,\text{cm}^{-1}$ in stoichiometric SiO_2. Thus the frequency of the stretching vibration can provide information about the degree of stoichiometry of the grown film. The absorption peak at $1076\,\text{cm}^{-1}$ for thermally- and plasma-oxidized film in Fig. 3 indicates the formation of SiO_2 of satisfactory stoichiometry with low strain density.

The chemical etch rate of the oxide was compared with that of thermal oxide to evaluate the densification of the films. P-etchant ($\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$, 1.5 : 1 : 30) is conventionally used as a sensitive etchant for the above purpose. The etch rate of as-grown oxide film measured in this solution is very high compared to that of $0.2\,\text{nm}\,\text{sec}^{-1}$ for thermal oxide film. This indicates a high porosity in as-grown oxide film. The etch-rate behaviour has been seen to improve systematically with increasing post-oxidation anneal temperature as shown in Fig. 4. Annealing in nitrogen at 900° C for 20 min resulted in an etch rate of $0.22\,\text{nm}\,\text{sec}^{-1}$ which is very near to that of the value for thermal oxide.

X-ray photoelectron spectroscopy (XPS) of the oxide has been carried out to investigate the chemical structure of the film by exploiting the shift of core-level binding energy during chemical bonding. XPS was performed at 10^{-10} torr in an ESCA/AES system (Physical Electronics 550) using X-rays from a MgK_α source with an energy of 1253.6 eV. The resolution of

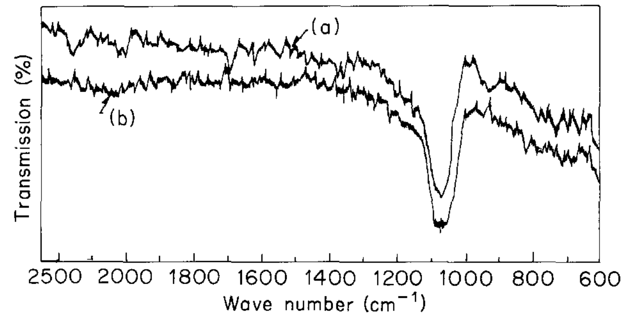

Figure 3 Infrared transmission spectra for silicon oxide. (a) Microwave plasma oxide, (b) thermal oxide.

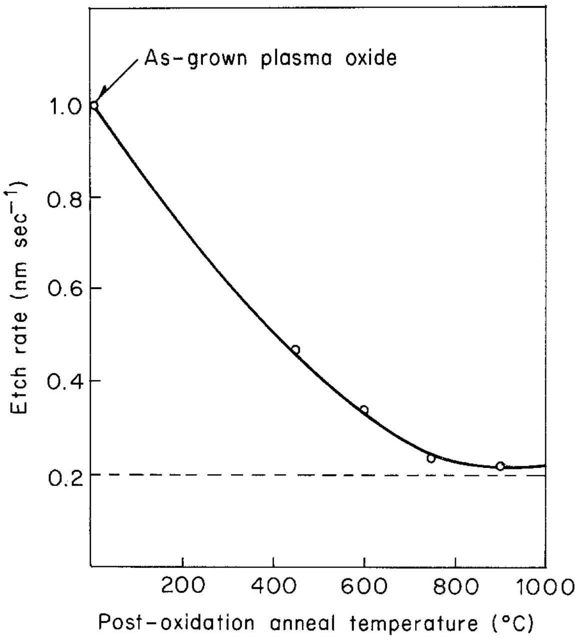

Figure 4 Relation between etch rate and post-oxidation anneal temperature after annealing in N_2 for 20 min. Dashed line, etch rate of thermally oxidized SiO_2 (1050° C).

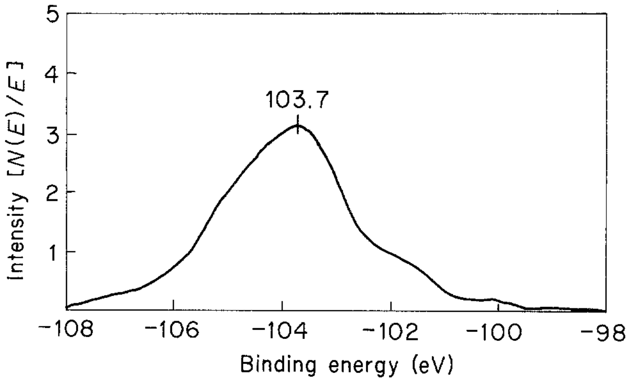

Figure 5 Silicon 2p photoelectron spectrum for microwave plasma-oxidized silicon.

the system is 1 eV, with an accuracy of 0.1 eV, and the measurements were taken with the area sensitivity factor for silicon (2p) as 0.17. The spectrum for silicon 2p electrons for the plasma-grown oxide is shown in Fig. 5 with a peak at 103.7 eV. This shows a shift in the binding energy value of 4.7 eV for 2p electrons from pure silicon. The value differs from that of the other possible compounds of silicon and oxygen [13], that is, SiO (102.5 eV) and Si_2O (100.9 eV). This value is close to the thermal oxide value of 103.4 eV. The XPS studies thus confirm the growth of a stoichiometric SiO_2 films in a microwave oxygen plasma.

The electrical and interfacial properties of the plasma oxides were characterized by capacitance against voltage (C–V) measurements made on MOS capacitors fabricated using oxides grown in the microwave discharge. Measurements were made with an HP–4061 semiconductor test system at a frequency of 1 MHz using an aluminium metal electrode on grown oxide. The parameter extracted from the high frequency C–V curve shows the value of fixed charge density (Q_f/q) of 2.4×10^{11} cm^{-2} for as-grown oxide. This high value indicates that post-oxidation annealing in inert atmosphere is necessary to lower the oxide charge levels. The value of Q_f has seen to be reduced continuously with an increase in post-oxidation annealing temperature in Argon atmosphere. Annealing at 900° C for 15 min in the above ambient reduced the Q_f/q value to 6.4×10^{10} cm^{-2}. The dielectric breakdown field of the oxide was in the range of 3 to 5×10^6 V cm^{-1} and is thus an indication of the moderately good dielectric strength of the plasma oxidized film. A comparison of the properties of microwave plasma oxides grown by different authors is presented in Table II.

4. Conclusions

The experimental results described in this paper show that silicon can be oxidized rapidly in electrodeless microwave oxygen plasma at a much lower temperature compared to thermal oxidation. The oxide growth behaviour can be explained by a parabolic rate equation. The growth is limited to certain pressure range and is sensitive to chamber configuration. This limitation can be removed by using a magnetoactive plasma which gives a high electron density over a wide pressure range. Structural characterization techniques like infrared and XPS spectra show the formation of perfectly stoichiometric silicon dioxide with low strain density. An improvement in the degree of densification and surface-charge density has been observed on annealing. However the breakdown field of the oxide needs to be improved. It would be of interest to study the effect of the incorporation of a source of chlorine in the oxygen gas stream to improve the quality of the interfacial property for acceptable use as gate oxides for MOSFETs.

Acknowledgements

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TABLE II Comparison of properties of microwave plasma grown oxides

References	Etch rate (p-etch) nm sec^{-1}	Refractive index	IR Spectra (Si–O stretching bond) (μm)	Si-2p electron binding energy (eV)	Breakdown field strength (V cm^{-1})	Q_f/q (cm^{-2})
Ligenza [6]	–	1.47	–	–	1×10^7	–
Kraitchman [7]	0.20	1.47	9.3	–	$3\text{–}7 \times 10^6$	–
Kimura [8]	0.25	1.47	9.3	–	–	–
Musil [10]	–	1.46	–	–	10^6	9.5×10^{11}
Roppel [9]	–	–	–	–	6.3×10^6	1.0×10^{11}
This study	0.22	1.45–1.47	9.3	103.7	$3\text{–}5 \times 10^6$	6.4×10^{10}

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