An electron paramagnetic resonance study of defects in PECVD silicon oxides

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Electron paramagnetic resonance (EPR) has been used to determine how the type and population of paramagnetic defects are altered firstly by changes to the composition of oxides grown on silicon by plasma enhanced chemical vapor deposition (PECVD) and secondly by subsequent anneal treatments of the various oxide films. Silicon oxide films with refractive index, \( n \), of 1.464, 1.487, 1.508 and 1.536 and thickness of 1 \( \mu \)m to 3 \( \mu \)m were studied; those of higher index have a higher silicon content. Only \( E' \) centers are detected in films with \( n = 1.464 \) and 1.487. Raising \( n \) to 1.508 leads to the introduction of other types of paramagnetic centers and a large increase in the average total spin concentration. Increasing \( n \) further to 1.536 produces a further small increase in average spin concentration. Identities are proposed for the additional types of defect and the dependence of their population on anneal temperature is also reported.

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1. Introduction
Amorphous silicon oxide is widely used as an insulating film in silicon-based electronic circuits and one of the methods for producing these films, which is attractive because it is a low temperature process, is plasma enhanced chemical vapor deposition (PECVD). High quality films, with a stoichiometry very close to that of SiO\(_2\) can be grown by this process [1–3] and such films would normally be used. Sometimes, however, it is desirable to use non-stoichiometric films which are silicon-rich (SiO\(_x\), \( x < 2 \)), for example, to improve hot carrier reliability of sub-micrometer MOS devices [4]. This improvement was related to the higher dangling-bond concentration in the modified oxide films which were thought to trap hydrogen. It is therefore of interest to know how the type and population of paramagnetic defects change as the amount of excess silicon is increased and this can be determined by the technique of electron paramagnetic resonance (EPR). EPR measurements have been made on defects in near-stoichiometric PECVD oxide [5–8], silicon-rich CVD [9, 10] and PECVD [4, 11] oxides and silicon-rich oxides prepared by other methods [12, 13]. However, with the exception of the work by Lin et al. [11] the experiments on PECVD oxides have usually only involved one or two oxide compositions. In this work EPR measurements are made on PECVD oxides of four different compositions and several thicknesses with a view to determining, in a systematic way, the effect of these changes on the type and concentration of paramagnetic defects in the oxide. The effect of annealing the films is also reported.

2. Sample preparation, composition and experimental techniques
The oxide films were grown by PECVD on boron-doped silicon wafers of resistivity 30–50 \( \Omega \)cm. The gases were SiH\(_4\) and N\(_2\)O. The deposition temperature and pressure were typically 350 °C on the wafer surface and 266 Pa, respectively. By varying the deposition pressure films were prepared with a refractive index, \( n \), measured at 633 nm with an ellipsometer, of 1.464 ± 0.001, 1.487 ± 0.001, 1.508 ± 0.001 and 1.536 ± 0.003. The film with \( n = 1.464 \) is closest to stoichiometric SiO\(_2\) and has a thickness of 2 \( \mu \)m. The other three types of film were each grown to thicknesses of 1, 2 and 3 \( \mu \)m. The increase in refractive index is, as found by Lin et al. [11], associated with an increase in the Si/O ratio. The growth of the films and refractive index measurements were carried out at Alcatel Microelectronics.

The EPR measurements were made at Trinity College at room temperature using a TM\(_{011}\) mode cavity operating at about 9.9 GHz; 100 kHz field modulation was employed. Spin populations were determined by comparing the area under the relevant spectrum with that for the spectrum of a Varian standard sample of pitch in KCl with a known number of spins. We estimate the absolute and relative values of the populations to be correct to within about ± 50% and ± 10%, respectively. \( g \) values were obtained by comparing the relevant field positions with that of a resonance with known \( g \) value—for example, that of F\(^+\) centers in MgO with \( g = 2.0023 \). The field range was calibrated with a proton NMR probe which also gave absolute field values.

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Some samples were subsequently annealed in argon for 10 min intervals at successively higher temperatures. After each anneal the sample was allowed to cool to room temperature and its EPR spectrum recorded.

3. Results and discussion

Fig. 1 shows that the shape of the EPR spectrum, which reflects the type of defects present, depends on the refractive index and hence on the composition and structure of the oxide. The smooth lines are computer-generated fits which match well the experimental spectra. We will now consider the results for each type of oxide film in turn.

The EPR spectrum of the most nearly stoichiometric oxide with \( n = 1.464 \) is asymmetric with a zero-crossing \( g \) value, \( g_0 \) of 2.0006 ± 0.0001. The computed spectrum, also shown in Fig. 1, is the powder pattern of a center with axial symmetry having \( g_{\|} = 2.0018, g_{\perp} = 2.0003 \) and it clearly fits well to the measured spectrum. The EPR spectrum of PECVD-grown SiO\(_2\) photoinjected with electrons [5, 6] has \( g_0 = 2.0007 \) and a shape very similar to that shown in Fig. 1a; it was shown to be due to \( \text{E}^0 \) center each corresponding to an unpaired electron in an sp\(^3\) hybridized orbital on a silicon atom backbonded to three oxygen atoms, \( \text{O}_3 \equiv \text{Si}^{+} \) (the dot represents an unpaired electron), and was suggested to be neutral [5, 6]. Devine [7] observed an EPR spectrum of as-deposited PECVD oxide with \( n = 1.485 \) (at \( \lambda = 632.8 \text{ nm} \)) which is also very similar to that for our oxide with \( n = 1.464 \); he fit the spectrum to that of a defect with an almost axially symmetric tensor with principal values \( g_1 = 2.0011, g_2 = 2.0002, g_3 = 1.9998 \) which he identified as being the \( \text{E}_1 \) center or at least \( \text{E}_x \)-like. The \( \text{E}_1 \) center can be represented as \( \text{O}_3 \equiv \text{Si}^{+} \).

\( ^{+}\text{Si} \equiv \text{O}_3 \) and is a positively charged oxygen vacancy [8] in amorphous SiO\(_2\); it is usually labeled \( \text{E}_x \). The close similarity between the spectrum in Fig. 1a and those described above and the fact that it easily saturates with increasing microwave power imply that it is certainly due to a type of \( \text{E}^0 \) center which may be \( \text{E}_x \)-like. The areal concentration of these centers (that is, the number per unit area of one face of the film) is \( 1.0 \times 10^{13} \text{ cm}^{-2} \). The oxide thickness is 2 \( \mu \text{m} \) so their average volume concentration is \( 5 \times 10^{16} \text{ cm}^{-3} \) comparable to the value \( \sim 2 \times 10^{16} \text{ cm}^{-3} \) found by Devine [7] in as-deposited oxide with \( n = 1.485 \).

The oxide films with \( n = 1.487 \) and thickness 1, 2 or 3 \( \mu \text{m} \) all give EPR spectra of the same shape with
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g_0 = 2.0012 \pm 0.0001 \text{ and peak-to-peak linewidth, } \Delta B_{pp} \text{ of } 0.31 \pm 0.01 \text{ mT which, as Fig. 1 shows, is different from that for the } n = 1.464 \text{ oxide. Although the spectrum saturates easily with increasing microwave power, as is typical of } \text{E}^0 \text{ centers, the spectrum cannot be fitted well to that of } \text{E}_x \text{ centers. Fig. 1b shows, however, that if the powder pattern of a defect with } g_{\|} = 2.0018, g_{\perp} = 2.0021 \text{ is superimposed on that for an } \text{E}_x \text{-like center with } g_{\|} = 2.0018, g_{\perp} = 2.0005 \text{ a reasonable fit can be obtained. The parameters of the former center are almost identical to those of the } \text{E}_x \text{ center (} g_0 = 2.00168, g_{\perp} = 2.0020 \text{) which have been associated with an oxygen deficiency in SiO}_2 \text{[14, 15]. Given the number of parameters involved the fit is uncertain but what is definite is that } \text{E}^0 \text{ centers are again present and that some or all of them differ from the } \text{E}_x \text{-like centers in stoichiometric PECVD oxides. The total } \text{E}^0 \text{ areal concentration in the } n = 1.487 \text{ oxide films of thickness 1, 2 or } 3 \mu \text{m is } 1.4 \times 10^{13}, 2.1 \times 10^{13} \text{ or } 2.2 \times 10^{13} \text{ cm}^{-2}, \text{ respectively. The fact that their areal concentration increases less rapidly than the oxide thickness implies that some or all of them are concentrated at one or both of the film interfaces. This is consistent with the finding that } \text{E}^0 \text{ centers in as-deposited PECVD SiO}_2 \text{ are mainly near the oxide/air interface} \text{[8]. The average volume concentration of the } \text{E}^0 \text{ centers in the } n = 1.487 \text{ oxide is in the range } \langle 7-14 \rangle \times 10^{16} \text{ cm}^{-3}. \text{Fig. 1c shows that the } n = 1.508 \text{ oxide film has a very different EPR spectrum from that of the films with lower } n \text{ values. Three features, A, B and C, are apparent and there are reasons for believing that each is associated with a separate resonance. Firstly, increasing the film thickness from 1 \( \mu \text{m} \) to 3 \( \mu \text{m} \) causes features A and B to increase more than C and, secondly, annealing leads to a reduction in C at a slightly lower temperature than for A and B. Thirdly, feature A appears to saturate less easily than B or C with increasing microwave power. Fig. 1c shows that a good fit can be obtained by the superposition of three lines with parameters \( g = 2.0016 \pm 0.0001, \Delta B_{pp} = 0.43 \pm 0.02 \text{ mT} \) (C), \( g = 2.0039 \pm 0.0001, \Delta B_{pp} = 0.37 \pm 0.04 \text{ mT} \) (B) and \( g = 2.0055 \pm 0.0008, \Delta B_{pp} = 0.8 \pm 0.2 \text{ mT} \) (A). The average total spin density is \( 8 \times 10^{17} \text{ cm}^{-3} \) considerably larger than for the films with lower \( n \) values. The fit yields spin densities of
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\begin{align*}
6 \times 10^{17} \text{ cm}^{-3}, & \quad 0.7 \times 10^{17} \text{ cm}^{-3} \text{ and } 1.3 \times 10^{17} \text{ cm}^{-3} \text{ for the lines with } g = 2.0016, 2.0039 \text{ and } 2.0055, \text{ respectively. Although the uncertainty of the fit makes these individual values also uncertain it is clear that the dominant spectrum is the one with } g = 2.0016 \pm 0.0001.
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![Figure 1](image-url)