ISSN 1330–0008
CODEN FIZAE4

EPR STUDY OF HYDROGEN-RICH SILICON OXYNITRIDE FILMS

BRANKO PIVAC*, BORIS RAKVIN*, ALESSANDRO BORGHESI** and ADELE SASSELLA***

*R. Bošković Institute, P.O. Box 1016, HR-41000 Zagreb, Croatia
**Dipartimento di Fisica, Università degli Studi, I-41100 Modena, Italy
***Dipartimento di Fisica "A. Volta", Università degli Studi, I-27100 Pavia, Italy

Received 7 April 1995

Revised manuscript received 12 June 1995

UDC 538.93

PACS 68.10.Cb, 68.55.Ln

We studied hydrogen rich silicon oxynitrides deposited from nitrous oxide and silane gas mixture by a plasma enhanced chemical vapour deposition apparatus on single crystal silicon substrates. Annealing study showed that hydrogen outdiffusion depends on the film composition and is particularly retarded for oxygen content $x = 1.4$. EPR analysis demonstrated that this film contains the highest concentration of D centres. However, the maximum concentration of charged dangling bond-like centres does not coincide with D centres. Therefore, we conclude that D centres act as hydrogen traps and are responsible for the peculiar hydrogen behaviour observed in the studied films.

1. Introduction

At the beginning of metal-nitride-oxide-silicon (MNOS) nonvolatile memory technology, the presence of oxygen in the silicon nitride was considered undesirable. This caused abandoning of atmospheric–pressure chemical vapour deposition technology in the favour of low–pressure chemical vapour deposition of silicon nitrides. Later Kapoor et al. [1] proposed that a small amount of oxygen in silicon nitride for MNOS devices is desirable, since it may trap electronic charges. Recently, silicon oxynitride has become a focus of investigations for applications in tunnel metal-insulator-silicon diodes [2], as interlevel dielectric for multilevel metallization structures [3], in local oxidation of silicon [4], and as final passivation layers [5]. It has been also explored as a replacement for silicon nitride in the MNOS structure [6].

At present, silicon oxynitride insulating films are considered interesting for applications in the integrated circuit technology due to their low intrinsic stress and good diffusion barrier properties. Since good insulating properties of the films are also needed, the nature and the density of the electrically active point defects must be studied.

One of the very important impurities often present in the material is hydrogen, whose behaviour certainly effects electrical performance of the film. It has been established that hydrogen is present typically in Si-H and N-H bonding configurations, of which the Si-H bond strength is the smallest. A correlation exists between the concentration of Si-H bonds and electrical parameters such as equilibrium positive charge and charge transport [7,8]. It has been suggested that silicon dangling bonds formed during film deposition and/or during subsequent thermal treatment give rise to an increase in charge transport [9,10]. This finding has been also confirmed theoretically [11]. This illustrates the importance of hydrogen chemistry in the oxynitride films for the electrical behaviour of MNOS structures.

Here, besides nuclear techniques used for film stoichiometry and composition characterization, and optical methods not reported here, we applied electron paramagnetic resonance (EPR) spectroscopy to study paramagnetic active defects in the films (silicon dangling bond being a typical example) and their dependence on the film composition.

2. *Experimental*

p-type Czochralski silicon wafers <100> oriented, with a 16-24 Ωcm resistivity, were used as substrates for the deposition of different films. All the substrate wafers, 150 mm in diameter and 765 μm in thickness, were back-lapped. Silicon oxynitride films about 5×10^{-5} cm thick were deposited at a temperature of 350 °C using a single wafer cluster deposition, plasma-enhanced, chemical vapour deposition (PECVD) system [12]. The parameters of the process are given in Table 1, together with the results of thickness and deposition rate measurements. Particular care was taken in choosing the deposition time to obtain films with comparable thickness. All films have been grown at SGS-Thomson, Agrate, Italy.

EPR measurements were performed employing a Varian E-109 spectrometer operating in the X-band (9.4 GHz). Some EPR spectra were recorded at 10° intervals of rotation of the magnetic field with respect to the Si (011) plane in order to reveal the dependence of the paramagnetic centres on the magnetic filed orientation. In order to improve the signal-to-noise ratio, signal averaging ($\approx$ 10 traces) was applied. The exact position of the g–factor and quantitative spin concentration was determined according to DPPH, and the detection limit of 10^{11} spins/cm^3 was achieved.

TABLE 1.
Samples a *to* f *are characterized by gas flow ratio* ($R = [N_2O]/\{[N_2O] + [SiH_4]\}$)*,* *thickness (d), and deposition rate (D. Rate).*

Sample	R	d in 10^{-8} cm	D. Rate in 10^{-8} cm/min
a	0.96	5105	9000
b	0.93	5183	11431
c	0.91	5063	12192
d	0.89	5043	12600
e	0.85	5260	13073
f	0.83	5267	13226

3. Results and discussion

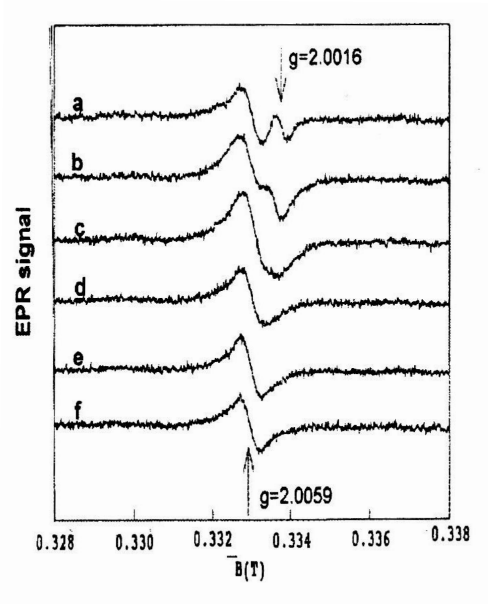
In order to determine the composition of the films, various techniques like: Rutherford backscattering, nuclear reaction and elastic recoil detection analysis have been applied and the results obtained are given in Table 2. Values for Si, O, N and H, given in Table 2, represent relative content of particular element, normalized to Si content taken as unity. As shown in the table, the samples represent a series with decreasing oxygen content and/or with increasing Si content if all elements were normalized to oxygen. The first in the series, the sample a, represents an almost perfect silicon dioxide SiO_2. Going further from sample b to sample f, oxygen content diminishes and, therefore, since nitrogen content is almost constant, its ratio to oxygen increases turning films from almost pure oxide to the nitride–like one. In the following we shall examine how this affects the defect population in the films.

The structure of PECVD silicon oxynitride is still a matter of a debate. Cros et al. [13] found from IR and EPR measurements that oxinitrides grown from N_2O and SiH_4 at ratio $R \leq 20$, which are considered to be rich in silicon, consist of two separate phases, SiO_xH_z and $SiN_yH_{z'}$. This implies different kind of defects present in the film, and it is of interest to reveal their presence and possible interaction with hydrogen. Behaviour of hydrogen in our samples, upon annealing, is somewhat peculiar. Namely, from optical studies [14] we found that hydrogen outdiffusion upon annealing at 600 °C, is retarded for sample **c** with respect to others. This behaviour could be attributed to the presence of other defects like dangling bonds interacting with hydrogen.

TABLE 2.
Relative content of O, N *and* H *in the samples* a *to* f, *measured by RBS, ERDA, and nuclear reaction analysis, reported as normalized to* Si *content.*

Sample	Si	O	N	H
a	1	1.8	0.2	0.1
b	1	1.7	0.3	0.3
c	1	1.41	0.24	0.19
d	1	1.2	0.2	0.2
e	1	0.95	0.19	0.19
f	1	0.91	0.18	0.18

To reveal dangling bond–type paramagnetic defects, we performed EPR measurements and the results obtained on as-received samples are shown in Fig. 1. One can immediately note one defect appearing in all films having $g = 2.0059$ which can



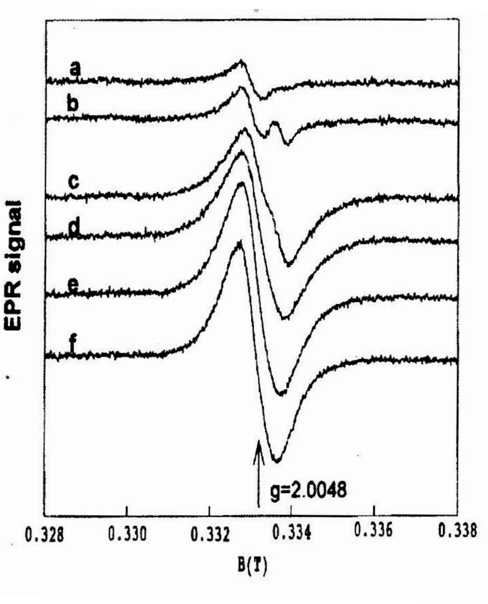


Fig. 1. EPR results for as-received samples. D centres (g=2.0058) and E' centres (g=2.0015) are indicated.

Fig. 2. EPR results for samples illuminated with UV light for 48 h *(right).*

be attributed to D centres often observed in amorphous silicon and/or to P_b defects observed at the Si/SiO_2 interface. D centres, i.e. dangling bonds at the silicon atom backbonded to three other silicon atoms, -Si$\equiv$Si$_3$, in amorphous silicon are isotropic upon rotation in magnetic field. On the other hand P_b centres, existing both on {111} and on {100} surfaces, show high asymmetry in magnetic field. In order to distinguish whether our signal comes from the defect structures within the film or from the interface Si-oxynitride film and/or from the edges cut prior to EPR measurements, we dipped our samples in buffered HF-HNO_3 solution, thus removing the effects of the edges. Moreover, we also took the spectra upon rotation in magnetic field for 10° and we observed no measurable asymmetry. Therefore, we conclude that the signal measured comes from the defects existing in as-received oxynitride films, and that it is due to D centres. Since we are dealing with silicon-rich films, it is not surprising to have silicon clusters that would give rise to this type of defect.

Another peak at about $g = 2.0016$ was observed in some of the spectra. This peak is attributed to the E' centres, often found in bulk SiO_2 material [15]. Since sample a shows an IR spectrum of almost pure silicon oxide, and other samples are rich in oxygen, it is reasonable to expect the existence of E' centres in this films. However, it should be noted that detectable concentration of E' centres decreases rapidly with decreasing oxygen content and for the last samples in the series it is not distinguishable, though all films have R ratio rather high, i.e. very high oxygen content.

All films were subsequently exposed to γ radiation from ^{60}Co source to the total dose of 10 Mrad. Spectra obtained after such treatment were qualitatively the same and therefore are not shown. The peaks existing in as–received samples, i.e. those due to D and E' centres increased for about 10% in intensity, and no new peaks appeared. This finding is, however, not in accordance with the current belief that those films should represent separated phases of nitride and oxide. If significant phase separation really existed, one would expect much more significant increase of E' centres upon exposition to γ radiation.

In the next step we exposed our samples to UV radiation from a high pressure mercury lamp and the results are shown in Fig. 2. From the figure we could observe different responses of the samples upon this treatment. While samples with very high oxygen concentration (samples a and b) showed only E' centre bleaching due to effect of UV irradiation, in all other samples a new centre with $g = 2.0048$ appeared. As the film is richer in nitrogen, i.e. as the relative content of nitrogen with respect to oxygen gets bigger, the new peak gets more intensive. This new peak behaves similarly as the K° centre [16].

The Si dangling bond, i.e. K° centre, is amphoteric and, when uncharged, it is paramagnetic [16,17]. The paramagnetic K° centres consist of an unpaired electron on Si atom bonded to three N atoms, and is characterized by values $g = 2.003$ and $\Delta B_{pp} = 1.15$ mT [18]. K^+ and K^- centres are diamagnetic. The K° centres could be generated by illuminating the material with UV light, with photon energy above 4.1 eV. These UV light induced paramagnetic centres that appear uniformly distributed over the thickness of the films. It has been suggested that the spin generation is caused by a change in spin and charge state of the pre-existing (diamagnetic) positively and negatively charged Si centres.

The centre we observed at $g = 2.0048$ has the same behaviour upon UV illumunation as the K centre. Similar centres were found in silicon rich nitride, and were attributed to -Si≡Si_2N [18]. However, since we are dealing with silicon-rich oxynitride both nitrogen and oxygen in various combination as backbonded atoms to silicon with dangling bond, various centres could coexist. Due to the insufficient resolution of EPR measurements, we are unable to determine the precise structure of the centres which are observed and the relative proportion in the observed signal.

With UV illumination, we could not reveal the existence (at least in measurable concentrations) of other nitrogen-related defects in the sample, such as overcoordinated N centres, or nitrogen bridging centres.

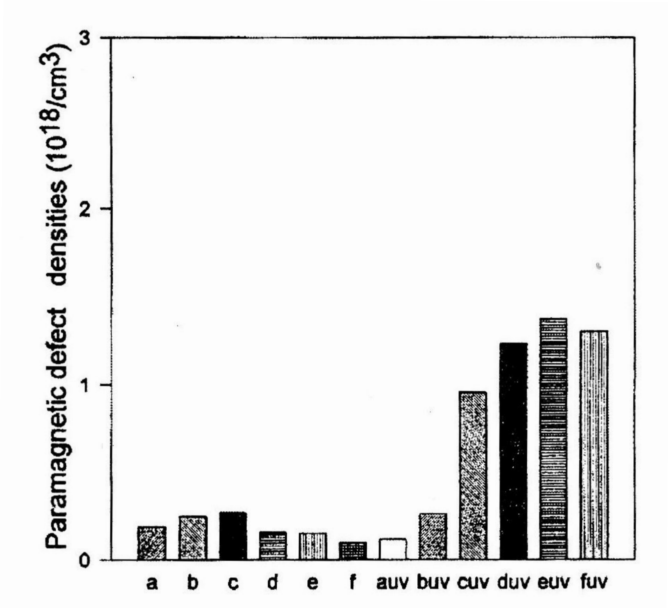


Fig. 3. Total concentration of paramagnetically active centres for as-received and UV illuminated samples.

However, it is very interesting to look at the total concentration of defects revealed by EPR measurements. Figure 3 shows that the maximum concentration of paramagnetically active centres in as-received films is found in sample c having a defect density of about 3×10^{17} defects/cm^3. This finding is quite unexpected: Since the silicon content in films gradually increases towards sample f, one would expect this sample to have the highest D centre concentration. This finding is not in favour of phase separation model of oxynitride films. Furthermore, the maximum in dangling bonds concentration observed for film **c** correlates well with the minimum for hydrogen outdiffusion due to thermal annealing, found by optical measurements [14]. The plausible explanation for this seems to be related to silicon dangling bonds, i.e. D centres present in the film act as a trap for hydrogen and therefore significantly reduce its diffusion. Further study is needed to understand the detailed behaviour of that process.

On the contrary, upon UV illumination, the maximum of defects was revealed in sample e, having about 1.5×10^{18} defects/cm^3. As shown, UV illumination revealed a quite different behaviour of various films upon such treatement. While in the first two films the change was not significant, i.e. for sample a UV illumination bleached about one third of defects and for sample b increase was only a slight, all other films showed fivefold increase in total paramagnetically active defect concentration. However, from hydrogen behaviour, we could conclude that only the D defect presence significantly influences hydrogen diffusion upon annealing, while other charged defects do not seem to play an important role.

4. *Conclusions*

We studied PECVD deposited hydrogen rich silicon oxinitride films formed from the specific gas mixture composition used, i.e. only nitrous oxide and silane. Upon annealing, the hydrogen present in the films shows a different behaviour for different films. In particular, it is shown that for film with oxygen content $x = 1.4$, hydrogen appears to be more stable incorporated in the film. Furthermore, EPR analysis revealed the same as-received film exhibits the highest concentration of D centres. A correlation between the two findings seems plausible, however more research is needed to understand the details of the interaction.

UV illumination, showed that the maximum of produced charged dangling bonds–like centres does not coincide with D centres, indicating, therefore, their minor effect on hydrogen diffusion.

References

1) V. J. Kapoor, R. S. Bailey and S. R. Smith, J. Vac. Sci. Technol. **18** (1981) 305;

2) R. Hezel, T. Meisel and W. Streb, J. Appl. Phys. **56** (1984) 1756;

3) V. S. Nguyen, S. Burton and P. Pan, J. Electrochem. Soc. **131** (1984) 2348;

4) W. K. Graham and J. C. Alderman, Physica **129 B** (1985) 224;

5) V. S. Nguyen, W. A. Landford and A. L. Rieger, J. Electrochem. Soc. **133** (1986) 970;

6) H. E. Maes and E. Vanderkerckhove, in *Silicon Nitride and Silicon Dioxide Thin Insulating Films,* edited by V.J. Kapoor and K. T. Hankins, (The Electrochem. Soc., Pennington, NJ, 1987) p. 28;

7) H. J. Stein, J. Electrochem. Soc. **129** (1982) 1786;

8) H. E. Maes and J. Remmerie, *Silicon Nitride Thin Insulating Films,* edited by V. J. Kapoor and H. J. Stein (The Electrochem. Soc. Pennington, NJ, 1983) p. 73;

9) H. J. Stein, J. Electron. Mater. **5** (1976) 161;

10) J. A. Topich and R. A. Turi, Appl. Phys. Lett. **41** (1982) 641;

11) J. Robertson and M. J. Powell, Appl. Phys. Lett. **44** (1984) 415;

12) J. Marks, K. Low, and D. Wane, Proc. Int. IEEE Conf. *VLSI Multilevel Interconnection* (IEEE, New York, 1989), p. 89;

13) Y. Cros, D. Jousse, J. Liu and J. C. Rostaing, J. Non-Cryst. Solids **90** (1987) 287;

14) B. Pivac et al., to be published;
15) D. L. Griscom, Nucl. Instr. Meth. B **1** (1984) 481;
16) J. Robertson, Phil. Mag. B **63** (1991) 47;
17) P. M. Lenahan, D. T. Krick and J. Kanicki, Appl. Surf. Sci. **39** (1989) 392;
18) D. Jousse, J. Kanicki and J.H. Stathis, Appl. Phys. Lett. **54** (1989) 1043.

ISTRAŽIVANJE SILICIJEVIH OKSINITRIDNIH FILMOVA BOGATIH VODIKOM METODOM EPR

Istraživali smo silicijeve oksinitridne filmove bogate vodikom, dobivene na monokristalnoj silicijevoj podlozi iz mješavine silana i dušik-(1)-oksida s pomoću uređaja za plazmom stimulirano kemijsko nanošenje iz pare. Proučavanje otpuštanja je pokazalo da izlaženje vodika ovisi o sastavu sloja, a posebice je usporeno pri sadržaju kisika $x = 1.4$. EPR mjerenja pokazuju da takav sloj sadrži najveću koncentraciju D centara. Zaključuje se da D centri djeluju kao zamke za vodik i uzrokuju neobična svojstva vodika u istraživanim filmovima.