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XPS study of SiO thin films and SiO–metal interfaces

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Abstract. X-ray photoelectron spectroscopy has been used to study the chemical structure of stoichiometric SiO thin films. The Si 2p line of silicon binding energy is found at 101.7 eV, and deconvoluted spectra show that at least four distributions of the type Si–($Si_{4-y}O_y$) exist in the films. The result is consistent with a random-binding model but differ from it for quantitative distribution.

The interfacial layer between the SiO thin film and a nickel electrode has also been investigated by the same technique. Chemical reactions are found to occur between the oxide and nickel ions to form silicides: Ni_2Si at the interface and NiSi deep inside the insulator. A probable diffusion of both Si and Ni atoms divides the insulator into two regions: one which is rich in Si at the interface and the other rich in SiO_2 in the insulator. The results obtained explain qualitatively some electrical properties of the metal–SiO–metal structures.

1. Introduction

Silicon monoxide thin films are widely used in electronic industry as dielectric materials, passivation layers, etc. It has been found that this oxide was formed on the silicon surface underneath the SiO_2 layer in the oxidation process of MOS structures and this has greatly increased the interest in its study (Hollinger 1987). In the past, the structure of silicon monoxide films has been discussed by using two different models: the random mixture model (White and Roy 1964, Temkin 1975, Johannessen *et al* 1975) and the random bond model (Philipp 1972, Senemaud *et al* 1974, Raider and Flitsch 1976, McCreary *et al* 1977, Finster *et al* 1985). The random mixture model states that the silicon monoxide does not exist in a single phase since it is formed by two components Si and SiO_2, whereas the random bond model is based on the five possibilities of bondings between the atoms of Si and those of oxygen. The fraction of the different distributions Si_yO_{4-y} obeys statistical laws; for stoichiometric SiO Philipp (1972) derived the following results: Si–Si_4 (6.25%), Si–Si_3O (25%), Si–Si_2O_2 (37.5%), Si–SiO_3 (25%) and Si–O_4 (6.25%). Different experimental data reported on silicon oxide films support both models but it can be pointed out that in most general cases, the composition of the oxides is not well known. On the other hand, only one type of analysis is generally carried out at the same time, so that it seems rather difficult to relate the results obtained to a defined oxide.

In this work, we report on x-ray photoelectron spectroscopy (XPS) measurements performed on silicon monoxide films on which several analyses have been carried out (Hoat and Nguyen 1976, Nguyen and Lefrant 1986a). The results obtained from these studies have shown on the one hand, that the films obtained by our method of evaporation are stoichiometric of formula SiO_x where $x = 1$, On the other hand, the x-ray emission,

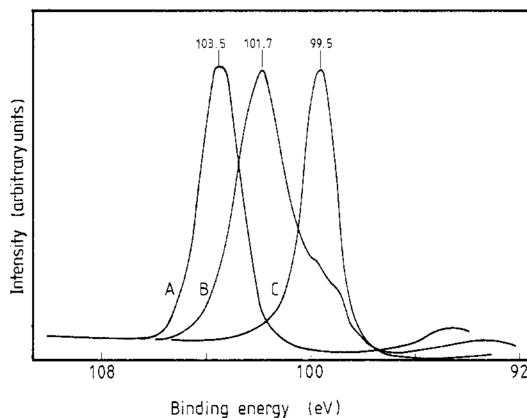

Figure 1. Si 2p lines: curve A, pristine SiO_2; curve B, SiO film; curve C, crystalline Si.

IR, Auger and Raman spectra of these films are quite different from those of silicon and silicon dioxide, whatever the kind of experiment. In particular, Raman scattering studies have suggested that some configurations of the possible Si–O bondings would be present in SiO films. Using the XPS technique, we have been able to identify the different basic structures of the SiO system and then to compare them with those proposed by the two models mentioned previously. Further study of interfacial layers between the oxide and metallic electrodes have also been carried out using the same technique in order to explain some electrical properties already reported on these films (Nguyen and Minn 1979, 1985).

2. Experimental details

Silicon monoxide thin films were prepared by evaporation of powder (supplied by Kochlight Laboratories Ltd) under high vacuum conditions ($<10^{-6}$ Torr) on aluminium or copper substrates. The temperature of the substrate was kept at 300 °C during the evaporation. The method of evaporation has been described in detail elsewhere (Hoat and Nguyen 1976). The thickness of the films was approximately 300 nm and the analysed surface was 5×5 mm^2. Al–SiO–Ni structures were prepared under the same conditions without breaking the vacuum.

XPS experiments were performed on a Leybold ESCA analyser (Université de Nantes—CNRS) under a vacuum better than 5×10^{-8} Torr and by using the Mg Kα radiation. Binding data were referenced to the Au $4f_{7/2}$ line (84 eV) of a gold plate fixed on the sample holder. Corrections of spectra displacement due to charging effects are also referred to this value. The data were processed by computer with smoothing, satellite subtraction, background subtraction and integration to determine the O:Si ratio.

3. Results and discussion

3.1. XPS measurements on SiO thin films

In order to characterise the bonding states of silicon and oxygen in SiO films, we compare their XPS spectra with those obtained from silicon single crystal and pristine silica.

In figure 1 Si 2p spectra of SiO_2, SiO thin film and Si are plotted as a function of the binding energy. The Si 2p lines of pristine SiO_2 (curve A) and crystalline Si (curve C)

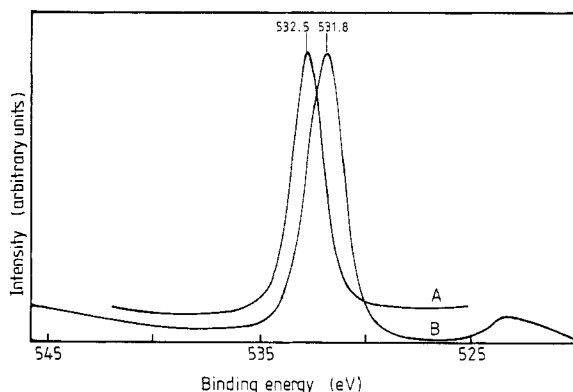

Figure 2. O 1s lines: curve A, pristine SiO_2; curve B, SiO film.

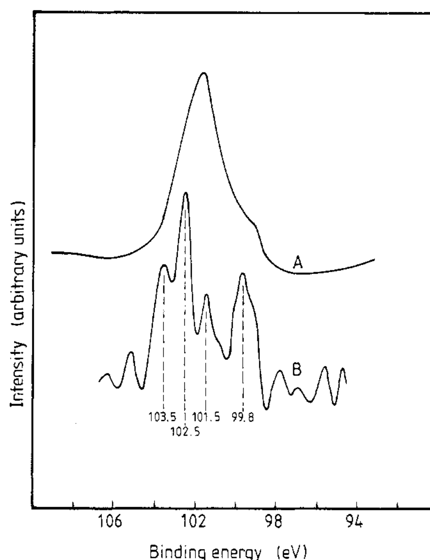

Figure 3. Curve A, experimental Si 2p spectrum of a SiO film; curve B, corresponding deconvoluted curve.

are located at 103.5 eV and 99.5 eV, respectively. The same line in SiO corresponds to a single line located at 101.7 eV reproducible within at most 0.3 eV with a full width at half maximum (FWHM) of about 2.3 eV (curve B). On the other hand, a shoulder with a binding energy similar to that of pure silicon (99.5 eV) is superimposed on the Si 2p line of SiO. In addition, we have shown in figure 2, the O 1s line of SiO_2 and SiO. The maximum of this line for the SiO film (curve B) is situated at 531.8 eV and differs from that of SiO_2 (532.5 eV, curve C).

The spectra obtained clearly show that the Si bonding in SiO cannot be attributed to that of SiO_2 but rather we can expect some kinds of tetrahedra to be formed in the film, especially those of free silicon which appear at lower binding energies. Thus, to make observation of these bondings possible we have deconvolved the spectra of the known instrumental function from the original spectra using the Van Cittert method. To eliminate unphysical features that may appear in deconvolved spectra, the following procedure was used: the spectra were recorded at a sufficiently high resolution, then background subtraction and smoothing were performed before deconvolution. In figure 3, a typical deconvolved curve of a Si 2p spectrum from a SiO film is shown. It can be seen that at least four peaks, respectively situated at 103.5, 102.5, 101.5 and 99.8 eV,

are present, the deconvolution being averaged over five measurements. From the linear interpolation approximation, these peaks would correspond to the following distributions (Raider and Flitsch 1976): Si–Si_4 (99.8 eV), Si–Si_2O_2 (101.5 eV), Si–SiO_3 (102.5 eV) and Si–O_4 (103.5 eV). The relative binding energies of the different components compared with the Si level are then 0, 1.7, 2.7 and 3.7 eV. The most intense peak occurs at 102.5 eV and would correspond to Si–SiO_3 distribution in SiO. The results differ slightly from those reported by Raider and Flitsch (1976) and Hollinger and Tran Minh Duc (1977), from whom the separation between the Si 2p lines in Si and SiO was 2.2 eV (compared with 2.7 eV in our spectra). However, we believe that the difference comes from the relative intensities of the peaks which could be explained on the one hand by inhomogeneities in the film, and on the other by differences in composition of the films. The composition of our film was SiO_x where $x = 1.04$; x was determined by electron microprobe analysis and confirmed by XPS (from the O 1s : Si 2p intensity ratio) on the analysed layer.

Similar multiple valence states of silicon were observed in the oxide layer formed on the silicon surface. In the case of the SiO_2–Si interface, Grunthaner *et al* (1979), using high-resolution XPS, show that the transition layer is composed of SiO, Si_2O_3 and SiO_2. Their chemical shifts from the Si 2p line of pure silicon are 1.7, 2.9 and 4 eV, respectively. Hollinger and Himpsel (1983, 1984), found comparable values in their work using a synchrotron radiation technique. In addition, they show another type of suboxide identified as Si_2O, the chemical shift of this component from the Si level being 1 eV. Similarly, an XPS study of the SnO_x–Si interface (Badrinaryanan *et al* 1986) indicates the presence of SiO, Si_2O_3 and SiO_2 with chemical shifts of 2, 3 and 4.2 eV, respectively, from the Si 2p line of pure silicon. These values are in good agreement with those obtained in SiO thin films from the above deconvoluted curves. It seems therefore that our SiO films have the same structure as one of the oxide formed on the Si surface at the first oxidation state.

The results are then consistent with our previous studies (Hoat and Nguyen 1976, Nguyen and Lefrant 1986) from which SiO thin films cannot be considered as a mixture of SiO_2 and Si. The bondings of Si atoms seem to be distributed according to the random bond model. However, we can make two remarks. Firstly, it should be noted that only four peaks are found in all the spectra, which could respectively correspond to the following distributions: Si–Si_4, Si–Si_2O_2, Si–SiO_3 and Si–O_4 (Raider and Flitsch 1976). The fifth distribution, Si–Si_3O, could not be identified and then would correspond to a very small fraction of tetrahedra in Si. It should be noted that such a species of oxide (Si_2O) has never been clearly identified by other analyses performed on SiO films. On the other hand, the results found here corroborate very well Raman scattering experiments performed on similar samples (Nguyen and Lefrant 1986). We have found in Raman spectra four possible Si_y–O_{4-y} distributions corresponding to four peaks located at 444, 454, 480 and 502 cm^{-1}. The two peaks located at 444 and 502 cm^{-1} are very intense while the other two are rather weak. The peak found at 480 cm^{-1} is identified to be related to amorphous Si clusters in the film. It would correspond to the Si 2p component with bonding energy located at 99.8 eV in the XPS spectra. Therefore, the oxide layer at the SiO_2–Si interface observed by XPS seems slightly different from the evaporated SiO film, since the distribution corresponding to Si–Si_3O bondings (Si_2O suboxide) was claimed to be found therein (Hollinger and Himpsel 1983, 1984). It seems, however, that the presence of Si substrate in the case of SiO_2–Si interface may modify the distribution of oxygen bonds at the immediate SiO transition layer and consequently, create oxygen deficient Si_yO_{4-y} tetrahedra. The results of Hattori and Suzuki (1983)

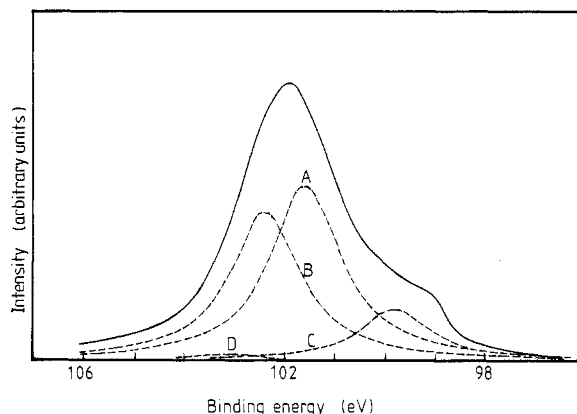

Figure 4. Energy distribution curve for the Si 2p line of the SiO film resolved into four components (see text for details): curve A, SiO; curve B, Si_2O_3; curve C, Si; curve D, SiO_2.

Table 1. Characteristics of the four Lorentzian functions used for the resolution of the Si 2p line of SiO_x and related distribution of the tetrahedra following the model of Philipp (1972) ($x = 1.04$).

Tetrahedron	Peak intensity (arbitrary units)	FWHM (eV)	Position of peak maximum (eV)	Theoretical distribution (%)
$Si-O_4$	210	1.3	103.2	5.3
$Si-SiO_3$	5940	1.4	102.4	27
$Si-Si_2O_2$	6965	1.4	101.6	37.4
$Si-Si_3O$	—	—	—	23
Si_4	2000	1.4	99.8	7.3

would support this explanation since they have found that the distribution involved was concentrated only in the abrupt transition layer between SiO_2 and Si. Similar conclusions have been recently established by Grunthaner *et al* (1987) from XPS study of the Si–SiO_2 system. A further complication is the very weak oxide thickness involved in the case of SiO_2–Si interface, the relaxation contribution to the binding energy shift may be quite different in this case (Finster *et al* 1985). The comparison between the two results is not then fully meaningful.

Secondly, the intensity of the peaks seem to indicate that the fractions of different distributions do not obey statistical laws as stated by Philipp (1972). Therefore, in order to estimate quantitatively the proportion of each species, we have proceeded in the resolution of the energy distribution curve into four components following the deconvolution result. The resolution was done using a Lorentzian function, the characteristics of which were computed to obtain the best fit of the experimental curve following the least squares minimisation method. The procedure was as follows: first, the peak energy positions were taken to be those found in deconvoluted curves, the two other parameters, i.e. intensity and FWHM, being arbitrarily chosen. After a run, all parameters (peak position, intensity and FWHM) were allowed to vary without limit until the best fit was obtained. In figure 4, we show the result of the decomposition, the characteristics used for this computation being given in table 1. The broken curves in figure 4 are the four components corresponding to the four possible Si–O bondings found in the deconvoluted spectra. It can be seen that the peak positions of the different curves are very close to those obtained from the deconvolution method. So, in view of the computed intensities,

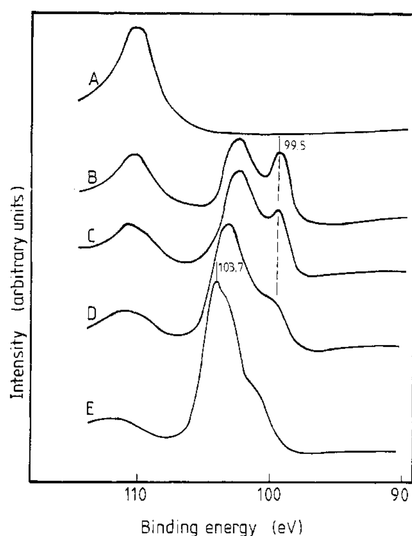

Figure 5. Evolution of the Si 2p line from the interface (curve A) to the inside of the oxide with successive removals of the nickel layer (curves B, C, D and E) (see § 3.2 for details).

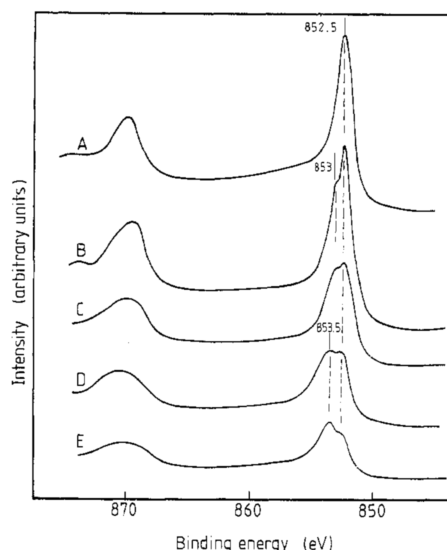

Figure 6. Evolution of the Ni $2p_{3/2}$ line from the interface (curve A) to the inside of the oxide with successive removals of the nickel layer (curves B, C, D and E) (see § 3.2 for details).

it is clear that our result contradicts the calculated values for the fractions of the distributions which are stated by the statistical model. We also note that there are two important components in the resolved curves (Si_2O_3 and SiO suboxides) that may be those found in Raman spectra of SiO thin film with peaks at 444 and 502 cm^{-1}.

3.2. XPS measurements at SiO–Ni interface

Electrical measurements in metal–SiO–metal structures have shown that a strong dependence upon polarity was observed either in thermally stimulated currents or in noise characteristics when near-noble metals (Ni, Pd, Pt) were used as electrodes (Nguyen and Minn 1979, 1985). Recently, the influence of such metals on AC conductivity have also been observed (Nguyen and Lefrant 1988) and from experimental data, it was found that the density of defects was sensibly reduced when using these metals in unsymmetrical structures (i.e. Al–SiO–Ni for example).

Since near-noble metals can react with silicon even at low temperatures (Scott *et al* 1983, Ottaviani 1986) to form silicides and since defects in SiO films are related to free silicon bondings, one can reasonably expect such a reaction to occur at an SiO–near-noble metal interface. So we have studied the bonding state of Si of a SiO thin film recovered with a layer of nickel by investigation of the Si 2p and Ni $2p_{3/2}$ XPS spectra. The following experimental procedure was used. The Ni $2p_{3/2}$ line was first recorded on the 'as-deposited' sample. Then, bombardment of Ar^+ ions at 1 kV was performed for a given time to remove the metallic layer step by step until the interface region is reached. The Si 2p and Ni $2p_{3/2}$ lines were then recorded and the process was repeated many times (Ar^+ ion bombardment and recording the spectra) throughout the thickness of the sample. We have not attempted to evaluate the depth profiling composition of the film.

Figures 5 and 6 show respectively the evolution of the Si 2p and Ni $2p_{3/2}$ spectra with successive removals of the nickel layer. The most striking feature of these spectra is the progressive formation of nickel silicides from Ni_2Si (peak energy at 853 eV) to NiSi

(peak energy at 853.5 eV) (Grunthaner *et al* 1980), this being progressive from the interface to the inside of the oxide. At the same time, the Si 2p line exhibits a shoulder corresponding to free silicon (99.5 eV) which diminishes in intensity with the growth of the NiSi phase. Finally, a change from SiO to SiO_2 is observed by the shift of the Si 2p line to higher energy (103.7 eV) when reaching the limit of the NiSi phase (curve E). We also note that the change of the Ni $2p_{3/2}$ line is gradual inside the oxide from the interface (where the first Si 2p signal is observed) up to about half the thickness of the sample (~300 nm). Beyond this limit, there is no further change of the Si 2p line; i.e. this line corresponds again to the stoichiometric SiO (101.7 eV) until the SiO–Al interface is reached (appearance of the Al 2s line at 72.8 eV).

From the above results, we can see that free silicon in SiO films reacts with the nickel layer in a manner similar to that at the interface of the Si–Ni system (Ottaviani 1986). The silicide Ni_2Si is first formed at the SiO–Ni interface by reducing the Si bondings, a proportion of nickel ions having possibly diffused through the interfacial layer inside the oxide to form NiSi here. Free silicon may also diffuse in the opposite direction (i.e. towards the interface) and leave behind regions rich of SiO_2. Marker experiments in the Si–Ni system (Tu *et al* 1975) have shown that the Ni ions may be transported across the interfacial layer and penetrate into the Si side even at low temperature.

The fact which may be surprising in view of the XPS spectra is the increase of the shoulder over the Si 2p line at the SiO–Ni interface. This cannot be attributed to the possibility of decomposition of the oxide under ion bombardment because the accelerating voltage was kept sufficiently low (no decomposition was observed in oxide films re-covered with a thin Al layer under the same conditions). On the contrary, Si ions may diffuse from the inside of the oxide to the interface region since Si bonds are supposed to be weakened by Ni (Cheung *et al* 1981).

We notice that such a reaction is not observed at the SiO–Al interface. It is known that aluminium does not form a silicide with silicon (Ottaviani 1986), but that eutectic phases can be formed at high temperatures. This is not the case with our structures, since the temperature of the substrate during evaporation is kept at 300 °C. However, we also note that reaction of aluminium with SiO_2 to give Al_2O_3 is found in some cases (Candela *et al* 1981, Derrien *et al* 1982). The thickness of the interlayer formed was estimated to be less than 0.5 nm (Candela *et al* 1981). It is then possible that we could not detect this layer, if any, in our experiment since the thickness of the layer removed after each erosion by ion bombardment is about 10 nm. Nevertheless, one can state that such a reaction, if it occurs, does not fundamentally modify the structure of the oxide as does the nickel layer.

These explanations would agree with data of electrical measurements from which the density of defects is found to be reduced by one or two orders of magnitude when using nickel as the electrode metal. As all Si bondings are not satisfied in SiO, they would act as charge traps in the semiconductor. Reaction with diffused Ni to form silicide then consumes a part of free Si and reduces the number of defects. Furthermore, at the SiO–Ni interface, accumulation of free Si would be the origin of rectification as observed in unsymmetrical Al–SiO–Ni structures (Nguyen and Minn 1979, 1985).

4. Conclusion

In conclusion, the experiments reported here give clear evidence that stoichiometric SiO thin films prepared by an appropriate evaporation method correspond to a stable

phase in which bondings between silicon and oxygen atoms are distributed according to the random bond model. The quantitative distribution of different kinds of tetrahedra is found, despite some discrepancies with the model of Philipp (1972) concerning the relative concentration of each species. We have also shown that chemical reactions between free silicon and nickel occur to form silicides in Al–SiO–Ni structures: Ni_2Si near the interface and NiSi deep inside the oxide. The accumulation of silicon ions at the interface and change of SiO into SiO_2 lead to the hypothesis that diffusion of either Ni or Si through the interfacial layer occurs by the same process as in the Si–Ni system. The results obtained give a satisfactory qualitative explanation of data of electrical measurements in SiO thin films published elsewhere (Nguyen and Lefrant 1988).

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