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Interface properties of hydrogenated amorphous carbon films on SiO_2 and $SiO_{1.2}$: an in situ photoelectron study

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The interface properties of hydrogenated amorphous carbon films (a-C:H) on silicon have been studied by an in situ photoelectron spectroscopy technique. Carbon layers have been deposited in situ on silicon oxide films, produced by ion beam oxidation (450 eV ion energy) and by thermal oxidation of Si(100), respectively. It is found that the ion beam oxidized silicon film contains contribution of lower oxidation states whereas the thermally oxidized silicon forms stoichiometric SiO_2. However, the photoelectron spectroscopy measurements revealed in both cases the formation of a mixed SiC/SiO_xC_y interface phase. The interface properties of the investigated a-C:H/silicon oxide systems could be correlated with the excellent adhesion properties of a-C:H films on SiO_2 substrates.

1. Introduction

Motivations for studying amorphous hydrogenated carbon (a-C:H) films stem from both their scientific interest [1,2] as well as technological applications. These films possess a variety of outstanding properties such as extreme hardness, chemical inertness and optical transparency up to 12 μm. These properties provide a-C:H films important applications in magnetic recording media [3,4], microelectronics [5–7], and optical components [8,9]. A few of the latest applications are protective coatings on lenses, sunglasses and watch-glasses as well as a-C:H deposition on razor-blades [10].

A primary concern in all applications of a-C:H films is adhesion. The quality of adhesion depends to a large degree on the properties of the interfacial layer that is formed between the overlayer and the underlying substrate. Earlier studies of a-C:H films on Si, GaAs, and Ge substrates have shown that the adhesion is strongly influenced by chemical bonding and atomic interdiffusion [11–13]. Good adhesion was found for these three substrate materials and was correlated with the formation of carbidic bonds at the interface.

The good adhesion of a-C:H films on SiO_2 substrates is well established. This adhesive behaviour of a-C:H films on quartz substrates lets presume the formation of an active interface. A detailed investigation of the a-C:H/SiO_2 interface becomes of particular importance specially in view of the fact that very often a-C:H films are deposited on Si substrates that are covered with a native oxide layer, with a typical thickness of 11–13 Å [14]. This is in the order of the thickness of our investigated oxide films (~ 15 and 35 Å) which have been produced by ion beam oxidation and thermal oxidation, respectively. Therefore the obtained results on the a-C:H/SiO_2 interface are also relevant for applications of a-C:H on Si. In the following we will show that the strong adhesion of a-C:H films on SiO_2 substrates is due to the formation of chemical bonds in the interface.

The ion beam oxidation of the silicon substrate resulted in the formation of silicon oxide films with contributions of lower oxidation states, and

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a stoichiometry of $SiO_{1.2}$ was obtained. The motivation for investigating the interface of a-C:H on ion beam oxidized $SiO_{1.2}$ films stems from the question whether the existence of lower oxidation states in the silicon oxide film could be responsible for the formation of other kinds of bonds at the interface. We could show that the bombardment with 400 eV carbon ions completely destroys this ab initio difference in stoichiometry, and that both interfaces are found to be very similar.

2. Experimental

Cleaning of the Si substrates was performed by sputtering with 5 keV Ar^+ ions with the substrate held at room temperature. Bombarding the Si substrate with 5 keV Ar^+ ions completely destroys the crystal structure at the surface. The cleanliness of the substrates was checked with photoelectron spectroscopy techniques. The silicon oxide films were then prepared in two different ways: by in situ oxygen ion bombardment of clean Si(100) substrates with a Penning ion source operated at an ion energy of 450 eV, and by thermal oxidation of Si(100). In order to perform the thermal oxidation (TO) the silicon was heated to 850°C for 5 min in 5×10^{-2} mbar pressure of pure oxygen. The as obtained silicon oxide films were then characterized using photoelectron spectroscopy. Contributions of lower oxidation states have been observed in the ion beam oxidized (IBO) silicon film [15], whereas the thermally oxidized silicon formed stoichiometric SiO_2. The a-C:H films were then deposited in situ with the Penning ion source operated with methane gas at an ion energy of 400 eV. The a-C:H deposition rate was of the order of low 10^{-13} m/s.

Because electron emission from the highly insulating SiO_2 films may cause charging problems, special care has to be taken in order to work with optimum film thickness for photoelectron spectroscopy measurements. These charging effects can be prevented by using thin films. In this case surface charging can be compensated by the injection of photoelectrons from the substrate since the penetration depth of the photons is much larger than the mean free path of the excited electrons, which is of the order of 1 nm. On the other hand, the film has to be thick enough in order to avoid the photoelectron spectra from being influenced by electrons originating from the substrate. Charging effects resulting in energy shifts of the order of about 0.3 eV have been observed in the He I and He II valence band (VB) spectra of the IBO silicon film. Due to a lower current density of the incoming photons, charging effects in the XPS spectra are smaller, of the order of the experimental error of the peak position (0.1 eV). The optimum thickness of the IBO Si is found to be about 35 Å. The thickness of the oxide layers was determined by calculating the intensity ratio of the Si 2p-oxide and the Si 2p-substrate core level peaks, assuming a SiO_2 escape depth of 3 nm for a photon energy of 1486.6 eV [15].

Photoelectron spectroscopy investigations were performed with a combined UPS/XPS/AES spectrometer EA11/100 by Leybold. The UPS spectra were measured in the constant retardation mode of 4 using He I ($h\nu = 21.2$ eV) and He II ($h\nu = 40.8$ eV) resonance lines. The energy resolution is 0.1 and 0.2 eV for He I and He II excitations, respectively. A satellite removal procedure was used to subtract the contributions from the He I and He II satellites [16]. The XPS core level data were measured with a monochromatized Al Kα X-ray source ($h\nu = 1486.6$ eV) and a spectrometer pass energy of 50 eV. For this case the energy resolution is about 0.6 eV. For all XPS measurements the energy calibration of the core levels was performed using a gold calibration sample and setting the Au $4f_{7/2}$ binding energy at 83.7 eV. Core level binding energy shifts were measured within an accuracy of 0.1 eV. A background subtraction was carried out for all XPS core level spectra.

The adhesive behaviour of a-C:H films on SiO_2 and $SiO_{1.2}$ was tested by scratching the a-C:H film (deposited about 1 year earlier) with a WC-pencil and performing the conventional scotch tape test. The a-C:H film could not be removed from the quartz film, which indicates the excellent adhesion properties.

3. Results

The UPS He I and He II valence band (VB) spectra of the clean silicon oxide (IBO) film (thickness ~ 35 Å) and a sequence of spectra measured after a number of deposition cycles are shown in figs. 1a and 1b, respectively. The VB spectra of the silicon oxide surface is dominated by three peaks at a binding energy of about 7.5 (peak a), 11.5 (peak b) and 15.5 eV (peak c, visible in the He II VB spectrum only). Peak (a) has been associated with the oxygen 2p nonbonding states occupied by a single pair of electrons. Peak (b) corresponds to O 2p (Si 3p, Si 3s) bonding states with mainly O 2p character due to the strong polarity of the Si–O bond [17,18]. Slightly different assignments have been given by Šimunek and Wiech [19]. They confirmed the O 2p-like character of peak (a), but in addition their X-ray emission spectroscopy (XES) measurements revealed the existence of Si 3p-like electrons. They have shown that Si 3p electrons contribute mainly to the energy region of peak (b) forming strong Si 3p–O 2p bonds. Moreover they found the contribution of Si 3s to peak (b) to be quite small (minimum of Si L-band). We observe marked differences in the valence band shape as measured with He I and He II excitation, namely an extra peak (peak c) and an increase in the relative intensity of the peak (b) as compared to peak (a) in He II. Both effects are due to a large extend to the analyzer transmission function, which is very low in this energy region.

The He I and He II VB spectra obtained after subsequent deposition of thin a-C:H layers reveal a gradual formation of an interface phase.

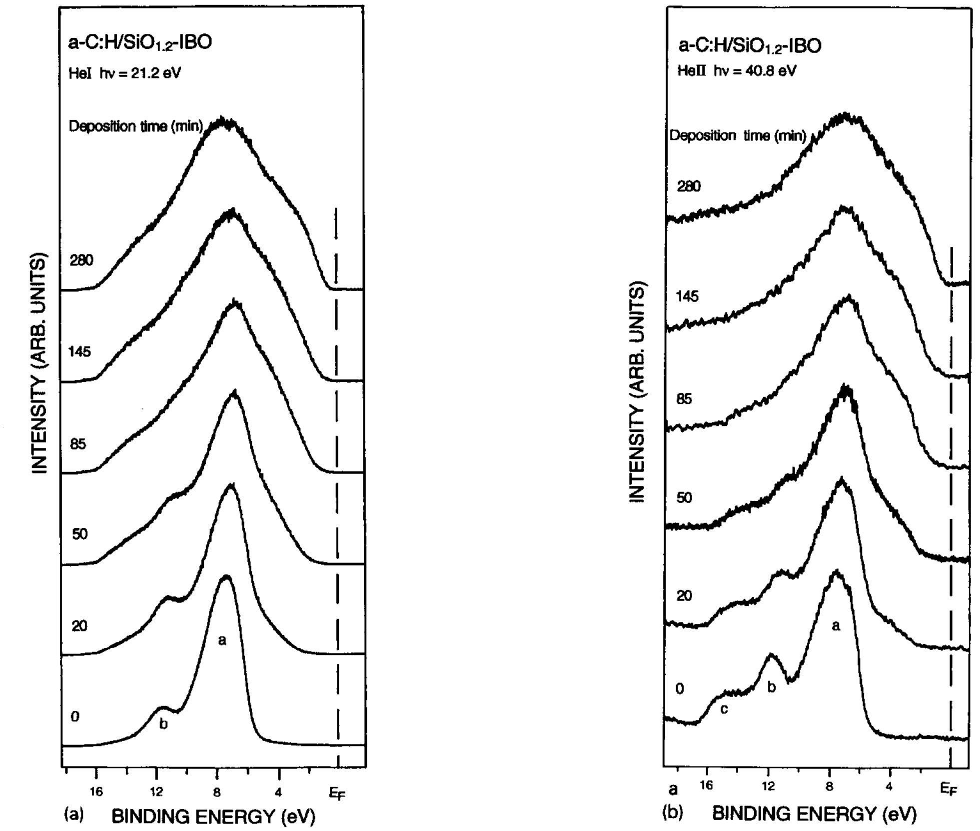

Fig. 1. UPS He I and He II VB spectra of clean ion beam oxidized silicon and a sequence of spectra measured after the indicated a-C:H deposition times. The topmost curves represent the VB spectra of a-C:H. The a-C:H deposition energy is 400 eV (room temperature deposition). All curves are normalized to the same peak height.

After a deposition of 20 min, which corresponds to a layer of about 2–3 Å, the most dominant effect is a contribution of electronic states near the Fermi level. This causes a shift of the VB edge towards the Fermi level from $E_F - E_V = 5.3$ eV to $E_F - E_V = 2.7$ eV. In addition peak (a) and (b) are shifted by about 0.3 eV towards lower binding energy. This shift is interpreted in terms of the disappearance of charging effects. With longer deposition times the photoelectrons emanate more and more from the overlayer. After about 280 min deposition time the He I and He II VB spectra are identical to that of bulk a-C:H [20].

Figs. 2a and 2b show the corresponding VB spectra of thermally oxidized silicon films (thickness ~ 15 Å) before and after sequential steps of a-C:H deposition. In contrast to the ion beam oxidized silicon a clear split of the nonbonding O 2p-states in two bands is visible in the thermal SiO_2 film. This two nonbonding bands at 6.1 and 7.3 eV binding energy correspond to nonbonding orbitals which lie perpendicular and parallel to a plane determined by the Si–O–Si-chain [21,22]. The spectra obtained after several deposition steps of a-C:H are similar to those obtained from the a-C:H/silicon oxide-IBO interface. This indicates a similar structure of the interface in both cases.

The Si 2p core levels are presented in figs. 3 and 4 for the ion beam oxidized silicon and the thermal SiO_2, respectively. All curves are normalized to the same peak height. The bottom curves correspond to a silicon oxide layer on the Si (100) substrate. The peak at 99.1 eV binding energy (peak A) is related to the pure Si substrate, while the second peak (peak B) at 103.3 and 102.8 eV (ion beam oxidized and thermally oxidized sili-

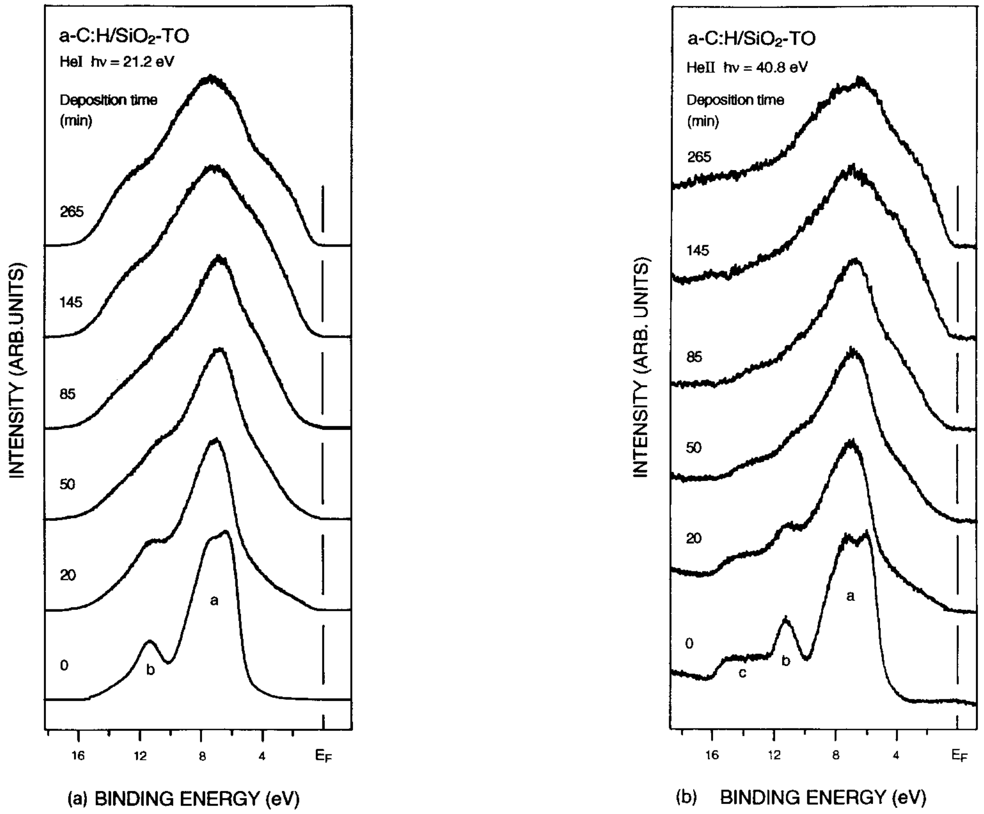

Fig. 2. UPS He I and He II VB spectra of clean thermally oxidized silicon and a sequence of spectra measured after the indicated a-C:H deposition times. The a-C:H deposition energy is 400 eV (room temperature deposition).

con, respectively) arises because of the charge transfer from Si to O following the Si–O bond formation. This effects a chemical shift to higher binding energy of the Si 2p core level [15].

From the positions of A and B we deduce a chemical shift of 4.2 and 3.7 eV for the IBO and thermally oxidized silicon, respectively. Various values of the chemical shift in SiO_2 as deduced from the position of A and B have been reported [23–26] and their origin has been a matter of controversy. On one hand it has been argued theoretically [25] and experimentally [23] that the charge transfer from Si to O in SiO_2 depends sensitively on the Si–O–Si bridging bond angle leading to a variation of the core level shifts. A testbed of this model was found in the variation of the core level shift as function of the Si–SiO_2 interface thickness, due to the compressive strain arising from the density mismatch between Si and SiO_2 which reduces the average value of the Si–O–Si bond angle (i.e. core level shift) to lower values near the interface. Such point of view has been refuted by Iqbal et al. [26] who explained the observed core level shifts as a function of thickness in terms of changes in oxidation process most likely due to the disruption of Si–O bonds. We investigated the dependence of the chemical shifts (as deduced from the positions of A and B in the Si 2p region as well as from the difference in binding energy of the O 1s and the Si 2p core level) in our IBO samples as a function of oxide thickness down to thicknesses of about 10 Å. Based on the fact that we could not ascertain any dependence of the chemical shift as a function of oxide thickness and that our two samples have

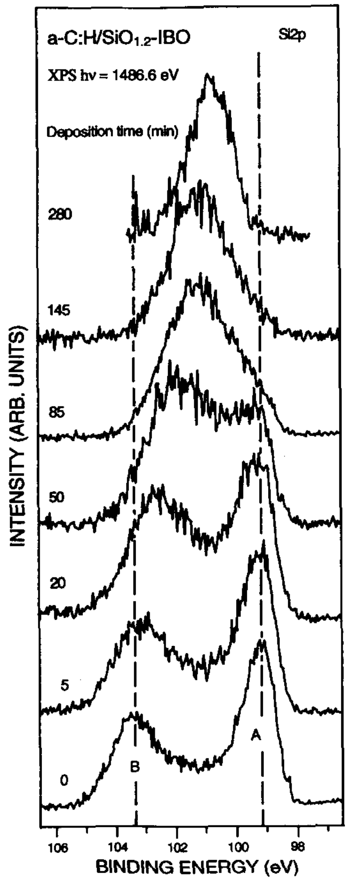

Fig. 3. XPS Si 2p core level spectrum of a clean $SiO_{1.2}$-IBO layer on a Si(100) substrate and a sequence of spectra after the indicated a-C:H deposition time in minutes. (All curves are normalized to the same peak intensity.)

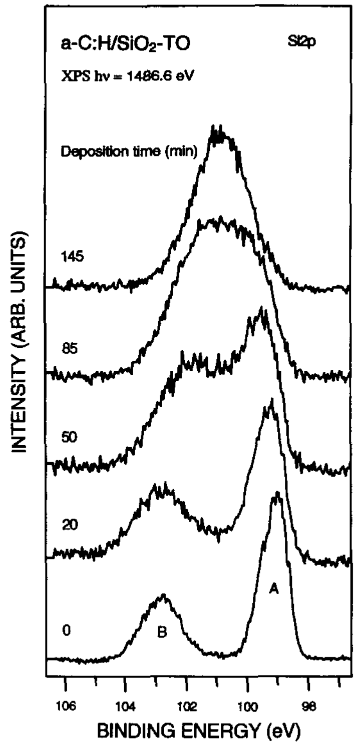

Fig. 4. XPS Si 2p core level spectrum of a clean SiO_2-thermal oxidation layer on a Si(100) substrate and a sequence of spectra after the indicated a-C:H deposition time.

been IBO prepared in one case and TO prepared in the other, we tend to agree with the latter point of view and believe the observed difference in the chemical shift is most likely due to changes in the oxidation process arising from different sample preparation. In addition, we observe contributions of intermediate oxidation states between peaks A and B, in the ion beam oxidized silicon film, as evidenced by the intensity buildup in the 100–102 eV energy region as compared to the TO sample. In fact the film stoichiometry as determined by the intensity ratio of the O 1s to Si 2p core levels, taking the contributions of the lower oxidation states into account and using the nominal SiO_2 stoichiometry of the TO film for calibration, is found to be close to $SiO_{1.2}$.

A decrease in intensity of peak A and a clear shift of the Si 2p-oxide level (peak B) to smaller binding energy with increasing coverage are visible in both sequences (figs. 3 and 4). We point out that at low coverages we obtain information mainly from the SiO_2 layer and Si substrate. With increasing coverage we sample the a-C:H/SiO_2 interface due to the limited escape depth of the photoelectrons. A detailed analysis of the top curve of fig. 3 (deposition time 280 min) which contains information of the interface will be given below.

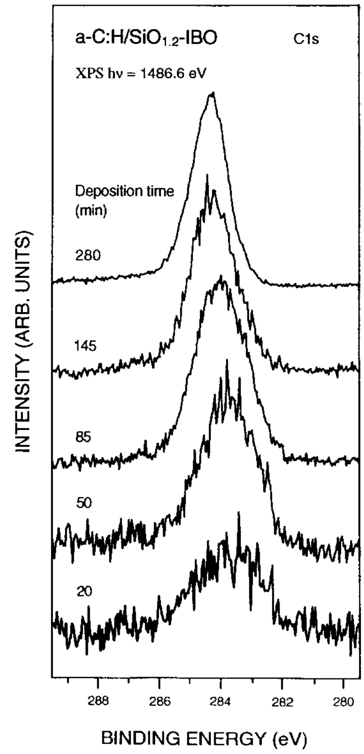

Fig. 5. XPS C 1s core level spectra measured after individual steps of a-C:H deposition on ion beam oxidized silicon.

The C 1s core lines are depicted in figs. 5 and 6 as a function of a-C:H deposition time. Information of the interface can be obtained from the C 1s core level at low deposition times, whereas the film properties themselves can be studied after prolonged deposition, when the film thickness has grown to a thickness that essentially all photoelectrons are originating from the a-C:H film. From the topmost curve a C 1s binding energy of 284.4 ± 0.1 and 284.5 ± 0.1 eV – a-C:H/$SiO_{1.2}$-IBO and a-C:H/SiO_2-TO, respectively – are obtained, the typical value for C in a-C:H [20]. We clearly observe a decrease in the line width of the C 1s core level with increasing deposition time.

The O 1s core levels are shown in figs. 7 and 8 for the ion beam and thermally oxidized silicon with different a-C:H coverages, respectively. The O 1s peak binding energy of the ion beam oxidized silicon amounts to 532.7 ± 0.1 eV, versus 532.1 ± 0.1 eV for the thermal stoichiometric SiO_2 (fig. 8) [27]. A close inspection of the photoemission O 1s line shape shows a symmetric line in the case of the TO film with a FWHM of 1.70 ± 0.05 eV, while that of the IBO is asymmetric and the FWHM amounts to 1.85 ± 0.05 eV. We assume that such asymmetry of the IBO O 1s line shape is the manifestation of the contribution of those intermediate oxidation states already mentioned when discussing the XPS Si 2p core level. After 20 min $C_mH_n^+$ bombardment the O 1s core level of the thermal SiO_2 film is shifted towards higher binding energy, to the same value of the O 1s binding energy in the ion beam oxidized silicon. A gradual shift toward lower binding energy is observed as function of increasing coverage, reaching a common value of 531.9 ± 0.1 eV in both cases for a deposition time of 145 min.

The binding energies of the Si 2p (280 min deposition time) and the C 1s (20 min deposition time) core level peaks cannot be explained by assuming a single phase (e.g. SiC) in the interface region. The most plausible explanation is to be found within a *two phases* model in the interface. Fig. 9 shows a least-squares decomposition of the Si 2p core level ($SiO_{1.2}$-IBO, 280 min deposition time) into two Gaussian functions. The binding energies of the two Gaussian peaks are located at 100.5 ± 0.2 and 101.2 ± 0.2 eV, which can be related to a SiC phase [11,28] and a SiO_xC_y phase, respectively. The assignment of the 101.2 eV value to a SiO_xC_y phase will be shown below, based on the position of the O 1s peak at high deposition times. The Gaussian FWHM corresponding to the SiO_xC_y phase amounts to 1.8 and that of the SiC phase to 1.3 eV. From the intensity ratio of the SiO_xC_y and the SiC peak we deduce that 48% of the whole Si 2p intensity is originating from the SiO_xC_y phase in the interface. Taking now the intensity ratio of the O 1s core level and 48% of the Si 2p core level (280 min deposition time, IBO interface, fig. 9), we get a value of

$$\frac{I^{\mathrm{O1s}}}{0.48 I^{\mathrm{Si2p}}} = 2.35.$$

The oxygen to silicon concentration can now be calculated using the cross sections of Scofield [29] and amounts to 0.5, which corresponds to a $Si_2O_1C_y$ phase in the interface.

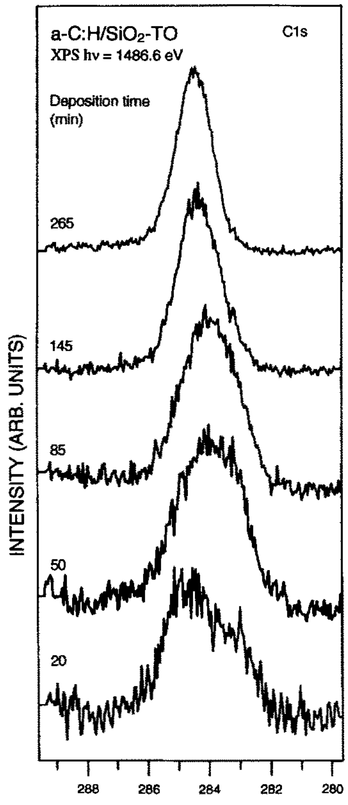

Fig. 6. XPS C 1s core level spectra measured after individual steps of a-C:H deposition on thermal SiO_2.

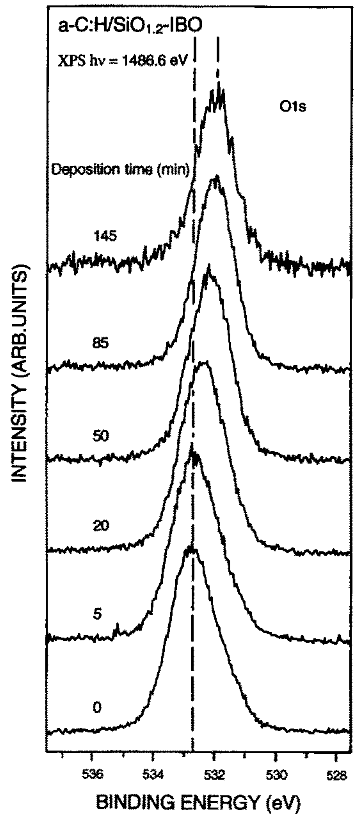

Fig. 7. XPS O 1s core level spectra of a clean ion beam oxidized silicon layer on a Si(100) substrate and a sequence of spectra measured after the indicated deposition time in min.

Another argument for the two phase model can be obtained from the data taken at shorter deposition times. In spite of the large scatter in the data, the film thickness being estimated to be about 2–3 Å, the C 1s core level spectrum after 20 min deposition time reveals an abnormal large line width. This could be explained by the super-

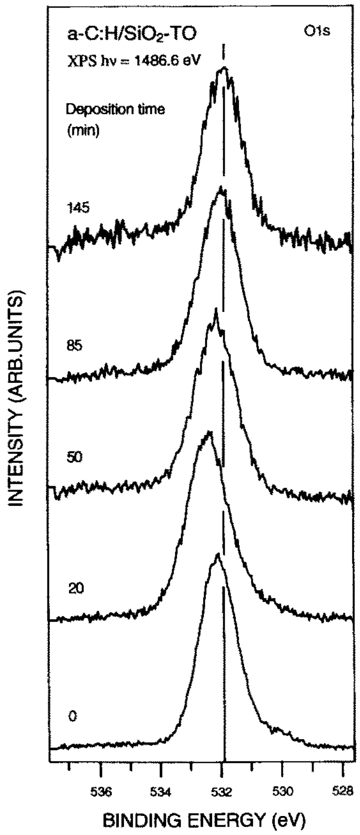

Fig. 8. XPS O 1s core level spectra measured after individual steps of a-C : H deposition on thermal SiO_2.

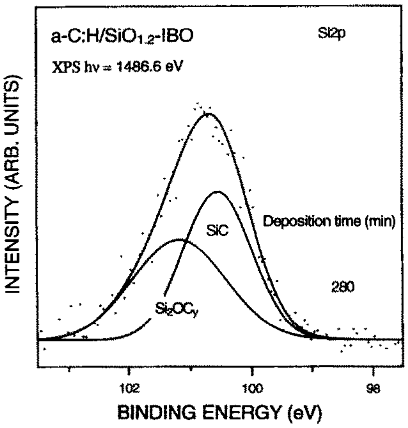

Fig. 9. Peak fit after the least-squares method of the Si 2p peak after an a-C : H deposition time of 280 min, a-C : H/$SiO_{1.2}$-IBO interface.

position of two contributions at least. The approximate binding energies of 283.1 ± 0.2 and 284.4 ± 0.2 eV in the a-C : H/$SiO_{1.2}$-IBO interface, and 282.9 ± 0.2 and 284.6 ± 0.2 eV in the a-C : H/SiO_2-TO interface, are suggestive of contributions from an a-C : H phase for the higher set of values (284.4 and 284.6 eV), and from a SiC phase for the lower set of values (283.1 and 282.9 eV). Our measured values of the C 1s binding energy in a-C : H and SiC amount to 284.4 and 283.1 eV, respectively [11]. In fact the presence of an a-C : H phase at very low deposition times has already been observed in the interface of a-C : H on Si and Ge [11,13]. A fit of the C 1s core level based on the model above is found to reproduce the data quite well, with however a slightly higher line width for the a-C : H contribution. The larger line width of the a-C : H contribution (1.9 eV as opposed to the accepted value of 1.5 eV in pure a-C : H) can be attributed to the presence of a third phase namely to the Si_2OC_y phase (already observed in the Si 2p region) in addition to the a-C : H and SiC phase. The a-C : H to SiC peak ratio amounts to 1.2 and 2.4 for the IBO and TO case, respectively. The higher amount of a-C : H in the TO interface as compared to the IBO interface (20 min deposition time) reflects the difference in deposition rate, which was about twice as high in the TO interface. The difference in deposition rate is estimated from the comparison of the variation of the Si 2p intensity as a function of deposition time. The Si 2p core level intensities become equal after a deposition time of 440 min for the IBO case and after 265 min for the TO interface case. From this comparison we deduce the TO deposition rate to be roughly about twice as high as the IBO deposition rate.

This model of a mixed SiC/Si_2OC_y phase in the interface is relied by our earlier investigations on ion beam deposition of the monomer hexamethyldisiloxan (HMDSO) at an ion energy of 270 eV [30]. By this technique a $Si_2O_{0.5}C_{2.8}$ phase was obtained with an O 1s binding energy of 531.9 eV, a C 1s binding energy of 284.2 eV and a Si 2p binding energy of 100.9 eV. The O 1s binding energy of the HMDSO film is in good agreement with the O 1s binding energy of our interface study. However, the Si 2p binding energy of the HMDSO film is about 0.3 eV smaller than those of the a-C:H/silicon oxide interface. With small amounts of oxygen in a SiO_xC_y film the binding energy of the Si 2p core levels will be close to the binding energy of SiC. With increasing oxygen content the chemical shift of the C 1s and Si 2p core levels increase [31]. We have already seen that the oxygen concentration in the $Si_2O_1C_y$ phase of a-C:H/$SiO_{1.2}$-IBO interface is about twice that in the HMDSO film. So the smaller binding energies of the C 1s and Si 2p core levels in the HMDSO film compared to our interface peaks are plausible. To get a further indication to the existence of the Si_2OC_y phase in the a-C:H/silicon oxide interface we performed an other experiment where we sputtered a SiC target with an argon–oxygen gas mixture, with variable oxygen content [31]. We prepared SiO_xC_y phases with different Si:O:C ratios. Interpolating the data we obtained a $Si_2O_1C_{2.2}$ phase with an O 1s binding energy of 532.0 ± 0.1 eV, a C 1s binding energy of 283.4 ± 0.1 eV and a Si 2p binding energy of 100.8 ± 0.1 eV. The observed differences in binding energies of the three investigated SiO_xC_y phases can be explained by the lack of hydrogen in the case of the sputtered SiC target as opposed to the HMDSO film and most probably to our interface phase. Based on our measurements, we can now conclude that the interface consists of a mixed SiC/Si_2OC_y phase.

The variation as a function of deposition time of the binding energy of peak B in the Si 2p region (see figs. 3 and 4) is depicted in fig. 10. The marked binding energy shifts indicate clearly that a chemical reaction between carbon and the substrate takes place in the interface region. The identical evolution of the chemical shifts in the a-C:H/$SiO_{1.2}$-IBO and a-C:H/SiO_2-TO interface is indicative of similar chemical reactions taking place at the interface. However the a-C:H deposition rate was higher by a factor of about two during the a-C:H/SiO_2-TO reaction, which explains the horizontal shifting of the two curves for higher deposition times. One point worth noting is the monotonic decrease of the Si 2p binding energy with increasing deposition time. A plateau value corresponding to a uniform interface phase is never reached since for times slightly higher than 440 min, all the photoelectrons originate from the overlayer a-C:H film and the Si 2p core level is no longer visible. Such behaviour is in contrast to that of the a-C:H/Si interface where a SiC interface formation was found to take place for subsequent deposition times before the Si 2p vanishes eventually at longer deposition times [11]. The trend here is rather the formation of a two-phase interface which gradually evolves from a predominantly Si_2OC_y phase at early deposition times to a SiC rich phase at later times. The relative intensity (area) ratio of the Si_2OC_y to SiC phase, obtained through the decomposition of the Si 2p core line into the Si_2OC_y and SiC phases (see fig. 9), is found to be about three times higher for a deposition time of 145 min as compared to 280 min (a-C:H/$SiO_{1.2}$-IBO interface).

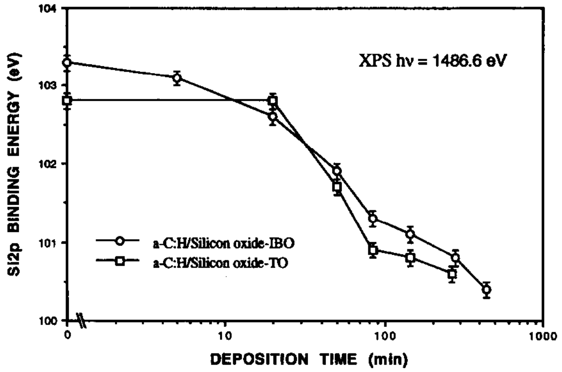

Fig. 10. XPS Si 2p peak maximum binding energies of the a-C:H/$SiO_{1.2}$-IBO and a-C:H/SiO_2-TO interfaces as a function of a-C:H deposition time.

Additional information can be obtained from the variation of the FWHM of the C 1s and O 1s core lines as a function of deposition time, as shown in fig. 11. Relatively wide lines are found at the beginning of the deposition process. The FWHM then decreases with increasing deposition time. The high value of the FWHM of the C 1s core level at low deposition time (20 min) is due to the superposition of three core lines originating from the SiC, Si_2OC_y and a-C:H phase, already mentioned above. The C 1s FWHM decreases with higher coverages because the photoelectrons originate essentially from the a-C:H overlayer only. Information about the silicon oxide layer are obtained from the O 1s core level at low deposition times. An enhanced width of the O 1s core line in the ion beam oxidized silicon film is observed due to the contributions of lower oxidation states. The line width is markedly lower in the stoichiometric thermal SiO_2 film. A decrease in the line width with increasing deposition time is also found for the O 1s core line. This indicates that the oxygen is built in the interface in a single phase.

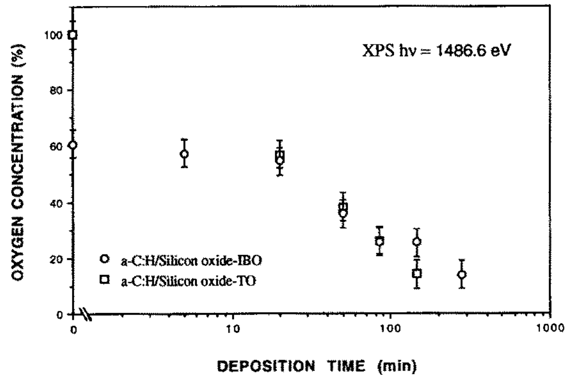

Fig. 12. Oxygen concentration as a function of a-C:H deposition time.

Fig. 12 shows the oxygen concentration as a function of deposition time. The oxygen concentration is calculated using the intensity ratio of the O 1s peak and peak B in the Si 2p region (see figs. 3 and 4). Assuming now that the thermally oxidized silicon forms stoichiometric SiO_2, we set the oxygen concentration in this case at 100% and normalize all other values by the same scaling factor. The marked lower oxygen concentration for the IBO silicon oxide sample reflects again the lower stoichiometry of 1.2 as compared to 2 in the TO sample. Again, information from the interface becomes accessible with increasing deposition time. So, the decrease in the oxygen concentration with increasing a-C:H coverage for higher deposition times reflects a decrease in the oxygen concentration in the interface itself. The effect of a decrease of the Si_2OC_y phase to the credit of the SiC phase towards the a-C:H overlayer has already been shown considering the Si 2p binding energy at high deposition times (145–440 min). The oxygen concentration of the a-C:H/$SiO_{1.2}$-IBO interface at high deposition time (280 min) amounts to 16%, whereas in the a-C:H/SiO_2-TO interface (265 min) the oxygen concentration amounts to 8% only. This fact can again be explained considering the growth rate of the a-C:H films which was higher by a factor of about two during the a-C:H/SiO_2-TO interface study. After an a-C:H deposition of 265 min on the thermal SiO_2 we get interface information at the a-C:H layer whereas the information about the a-C:H/$SiO_{1.2}$-IBO interface originates from a region closer to the silicon oxide film. We have already shown that the oxygen concentration in the interface decreases towards the a-C:H overlayer.

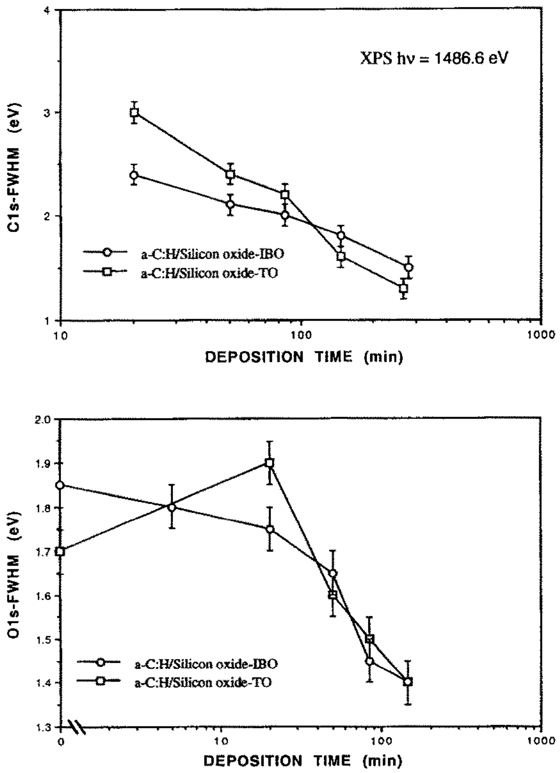

Fig. 11. FWHM of the C 1s and O 1s core lines of the a-C:H/$SiO_{1.2}$-IBO and a-C:H/SiO_2-TO interface as a function of deposition time.

4. Discussion and conclusions

The properties of the interface determine to a large extend the quality of adhesion of an overlayer on a substrate. Our investigations of the electronic structure of the a-C:H/SiO_2 interface have shown that there exists a strong interaction between the silicon oxide overlayer and the incoming $C_mH_n^+$ ions. The binding energies and the relative intensities of the Si 2p, C 1s and O 1s core levels lead to the conclusion that the interface consists of two phases, a SiC and a Si_2OC_y phase. Considering the intensity ratio of the O 1s and the Si 2p peak at high deposition times we obtained an oxygen concentration of 16% (a-C:H/$SiO_{1.2}$-IBO) and 8% (a-C:H/SiO_2-TO) in the interface. This oxygen is bound in a single Si_2OC_y phase. We have also seen that the concentration of the SiC phase increases with increasing interface thickness at the expense of the Si_2OC_y phase.

The penetration depth of 400 eV C^+ ions in SiO_2 amounts to 24 Å. The penetration depth was calculated with TRIDYN version 3.3 in the static mode. Assuming 10–20 strikes with SiO_2 molecules on average, the carbon ions would transmit 40–20 eV energy during each impact. The high bond strength in SiO_2 amounts to 799.6 ± 13.4 kJ/mol [32], which corresponds to 8.4 eV/bond. In the investigated case the ion energy of the incoming carbon ions is high enough to break the Si–O bond and form other compounds at the interface of SiO_2 and a-C:H.

Earlier interface investigations of a-C:H films on Si and Ge substrates have shown that good adhesion is combined with a reactive interface leading to an interface phase of a few nanometers, whereas poor adhesion is indicative of a passive interface as in the case of a-C:H on Au [33]. However an active interface formation is a necessary but not sufficient condition as demonstrated by the case of a-C:H on GaAs(100) [11], where adhesion of amorphous hydrogenated carbon on GaAs is poor in spite of a reactive interface. A breaking up of GaAs bonds is resulting in an As enrichment of the a-C:H/GaAs interface and is believed to be responsible for the observed poor adhesion of a-C:H on GaAs. In the case of a-C:H on SiO_2 no such decomposition has been observed, and the formation of a reactive interface gradually changing from silicon oxide to the a-C:H film starting with an oxygen rich phase and ending with a carbon rich phase has been found.

In conclusion, the interface properties of the investigated a-C:H/silicon oxide systems could well be correlated with the adhesion properties of a-C:H films on the SiO_2 substrates. It was found that chemical bonding and a gradual change in the interface are responsible for the strong adhesion of a-C:H films on SiO_2 substrates and silicon substrates covered with a native oxide layer.

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References

[1] J. Robertson, Adv. Phys. 35 (1986) 317.
[2] W. Möller, Appl. Phys. Lett. 59 (1991) 2391.
[3] H.-C. Tsai and D.B. Bogy, J. Vac. Sci. and Technol. A 5 (1987) 3287.
[4] C.J. Robinson, R.N. Payne and A.E. Bell, J. Appl. Phys. 64 (1988) 4646.
[5] A.A. Khan, J.A. Woollam, Y. Chung and B.A. Banks, IEEE Electron Devices Lett. 4 (1983) 146.
[6] A.A. Khan, J.A. Woollam and Y. Chung, Solid State Electron. 27 (1984) 385.
[7] M. Kakuchi, M. Hikita and T. Tamamura, Appl. Phys. Lett. 48 (1986) 835.
[8] S. Craig and G.L. Harding, Thin Solid Films 97 (1982) 345.
[9] B. Dischler, A. Bubenzer and P. Koidl, Appl. Phys. Lett. 42 (1983) 636.
[10] After abstracts of K.W.R. Gilkes, J. Robertson and D.M. Grant of the "Second European Conference on Diamond, Diamond-like and Related Coatings" in Nizza (1991).
[11] D. Ugolini, J. Eitle, P. Oelhafen and M. Wittmer, Appl. Phys. A 48 (1989) 549.

[12] M. Wittmer, D. Ugolini, J. Eitle and P. Oelhafen, Appl. Phys. A 48 (1989) 559.
[13] M. Wittmer, D. Ugolini and P. Oelhafen, J. Electrochem. Soc. 137 (1990) 1256.
[14] A. Licciardello, O. Puglisi and S. Pignataro, Appl. Phys. Lett. 48 (1986) 41.
[15] F.J. Himpsel, F.R. McFeely, A. Taleb-Ibrahimi and J.A. Yarmoff, Phys. Rev. B 38 (1988) 6084.
[16] G. Indlekofer, Systematics in the Electronic Structure of Polyvalent Liquid Metals Determined by Electron spectroscopy, PhD Thesis, Universität Basel, 1987.
[17] F.G. Bell and L. Ley, Phys. Rev. B 37 (1988) 8383.
[18] N. Binggeli, N. Troullier, J.L. Martins and J.R. Chelikowsky, Phys. Rev. B 44. (1991) 4771.
[19] A. Šimůnek and G. Wiech, Solid State Commun. 76 (1990) 955.
[20] P. Oelhafen and D. Ugolini, in: Amorphous Hydrogenated Carbon Films, Eds. P. Koidl and P. Oelhafen (Les Editions de Physique, Les Ulis, 1987) p. 267.
[21] T.H. DiStefano and D.E. Eastman, Phys. Rev. Lett. 27 (1971) 1560.
[22] S.T. Pantelides and W.A. Harrison, Phys. Rev. B 13 (1976) 2667.
[23] F.J. Grunthaner, P.J. Grunthaner, R.P. Vasquez, B.F. Lewis, J. Maserjian and A. Madhukar, Phys. Rev. Lett. 43 (1979) 1683.
[24] A. Ishizaka, S. Iwata and Y. Kamigaki, Surf. Sci. 84 (1979) 355.
[25] R.N. Nucho and A. Madhukar, Phys. Rev. B 21 (1980) 1576.
[26] A. Iqbal, C.W. Bates and J.W. Allen, Appl. Phys. Lett. 47 (1985) 1064.
[27] D. Ugolini, S.P. Kowalczyk and F.R. McFeely, J. Appl. Phys. 70 (1991) 3899.
[28] S.E. Hicks, A.G. Fitzgerald and S.H. Baker, Philos. Mag. B 62 (1990) 193.
[29] J.H. Scofield, J. Electron Spectrosc. Relat. Phenom. 8 (1976) 129.
[30] D. Ugolini and P. Oelhafen, private communications.
[31] S. Schelz, P. Gantenbein and P. Oelhafen, to be published.
[32] D.R. Lide, Ed., Handbook of Chemistry and Physics, (CRC Press, New York, 1991–1992) ch. 9, p. 108.
[33] D. Ugolini, Direct Ion Beam Deposition of Diamond-Like Amorphous Carbon Films (a-C:H) and Polymer-Like Films: In-situ Characterization by Photoelectron Spectroscopy, PhD Thesis, Universität Basel, 1989.