View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by Archipel - Université du Québec à Montréal

# Interface study of hydrogenated amorphous silicon nitride on hydrogenated amorphous silicon by x-ray photoelectron spectroscopy

M. Beaudoin, C. J. Arsenault, R. Izquierdo, and M. Meunier
*Groupe des Couches Minces(GCM) and Département de Génie Physique, Ecole Polytechnique de Montréal, C.P. 6079 Succ. "A", Montréal, Québec, H3C 3A7, Canada*

(Received 18 August 1989; accepted for publication 10 October 1989)

The interface between near stoichiometric hydrogenated amorphous silicon nitride ($a$-SiN$_x$:H) deposited on hydrogenated amorphous silicon ($a$-Si:H) is studied using x-ray photoelectron spectroscopy as a function of the electron escape angle. This method allows the study of $a$-SiN$_x$:H overlayers of about 40 Å thickness which is typical of the thicknesses used for well and barrier layers in superlattices and quantum well structures. Within the instrument's resolution, subnitride components constitute less than 1% of the interface bonds. It is therefore concluded that the interface is atomically abrupt.

The electronic and optical properties of amorphous semiconductor superlattices[1-4] and quantum well structures depend on the quality of the heterojunctions between the two amorphous semiconductor materials. The most extensively studied are superlattices, quantum well, and multiple quantum well (MQW) structures formed by alternating layers of hydrogenated amorphous silicon ($a$-Si:H) and hydrogenated amorphous silicon nitride ($a$-SiN$_x$:H). For example, quantum size effects,[5,6] resonant tunneling,[4,7] photoinduced enhanced conductance (PIEC),[8] and photoconductance[9] have been observed in such structures. The $a$-Si:H/$a$-SiN$_x$:H interfaces can be studied in superlattices by transmission electron microscopy (TEM) or x-ray diffraction.[10,11] Recently, Yang *et al.*[12,13] used photoelectron spectroscopy (PES) to show that this interface is atomically abrupt. Their approach consisted of growing several samples with thin overlayers ($\leqslant$10 Å) of $a$-Si:H or $a$-SiN$_x$:H grown on the complementary bulk material and studying these, as a function of overlayer thickness, with PES.

In the present letter, x-ray photoelectron spectroscopy (XPS) results are presented for a sample consisting of a near stoichiometric $a$-SiN$_x$:H overlayer, approximately 40 Å thick as determined from the growth rate, grown on bulk $a$-Si:H by glow discharge. Instead of producing several samples with different overlayer thicknesses, the interface of a single sample is probed by collecting data for different electron escape angles. This approach allows a better determination of the interface quality since the same interface is studied at different angles and is therefore not subject to inherent variability between samples. The XPS method uses higher energy photons (Mg $K\alpha$ x-ray source: 1253.6 eV) than the PES method (UV light: 125 eV) used by Yang *et al.* The electron escape length from XPS measurements is therefore longer and allows one to probe a deeper interface ($>$40 Å) while the PES method is limited to samples with overlayer thicknesses of about 10 Å. The thicker overlayer is more representative of actual conditions in superlattices, whereas very thin overlayers may be more sensitive to strain induced by the underlying bulk material.

A brief exposure to ambiant air causes oxidation in the first few monolayers of the samples. This is critical in PES measurements since this oxidation represents a large part of the overlayer and would complicate, or even prevent, the interpretation of the data. To circumvent this problem, Yang *et al.* transported their samples directly from the reactor to the PES chamber under ultrahigh vacuum so as to prevent any exposure to air. On the other hand, surface oxidation is not a problem in XPS studies since the region which is probed lies well below the first few monolayers. When the exposure is limited to a few minutes, XPS studies allow for straightforward characterization of the chemical bonding at the interface between the thin overlayer and the bulk material.

Figure 1 shows the spectra obtained when the Si $2p$ core levels are probed as a function of electron escape angle $\alpha$ for the $a$-SiN$_x$:H/$a$-Si:H interface. For every angle, two peaks are clearly distinguished. The peak at lower binding energy ($-$99.5 eV) is due to the Si $2p$ core level of Si bonded to four Si atoms (Si—Si$_4$) while the other peak ($-$101.9 eV) is due to the chemical shift of the $2p$ level when Si is bonded to four N atoms (Si—N$_4$).[13] This chemical shift comes from local charge transfer due to the electronegativity difference between Si and N atoms. The $2p$ core levels are doublets constituted of the $P_{1/2}$ and $P_{3/2}$ peaks, separated by 0.6 eV, which cannot be resolved in our spectrometer. In principle,

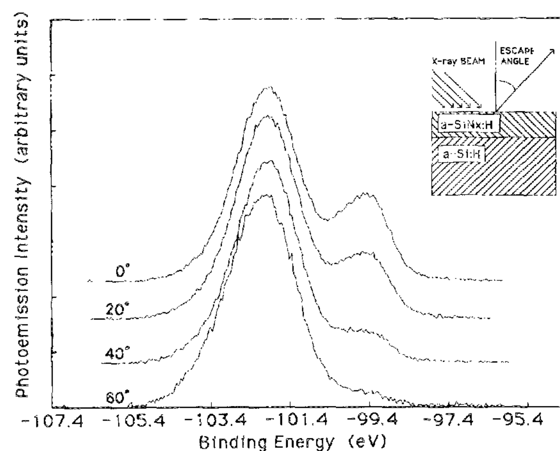


FIG. 1. XPS spectra as a function of electron escape angle. The peak at the lower binding energy ($-$99.5 eV) is the $2p$ core level associated with Si bonded to four Si atoms while the peak at the higher binding energy ($-$101.9 eV) represents the $2p$ level associated with Si bonded to four N atoms. The widening of the 60° peak is indicative of surface oxide contamination.

the $2s$ core levels, which are singlets, should therefore be easier to fit. It turns out that the $2s$ peaks are, however, wider than the $2p$ level peaks and are less well resolved.

Figure 2 shows a typical spectrum (at $\alpha = 0°$) which has been fitted using the two $2p$ core level peaks and imposing that the chemical shift, the full width at half maximum (FWHM), and the Gaussian–Lorentzian mixture be kept constant throughout the analysis at all angles. These restrictions help make the fits self-consistent since no XPS fits are absolute. The two peaks are added to reproduce the envelope spectra as shown by the continuous line through the spectrum of Fig. 2. This analysis was repeated for all angles. For larger $\alpha$, the presence of surface oxide was observed on the samples, as evidenced by the widening of the 60° peak on Fig. 1, and a peak with a chemical shift of 3.2 eV was included in the analysis for $\alpha \geqslant 40°$. Thus, even though all of the oxygenated species, from $N_3$-Si-O to Si-$O_4$, are expected to be present in native oxide, the chemical shift per Si— N bond (0.55 eV) determined here and that of 0.93 eV per Si—O bond, previously determined in our laboratory,[14] indicate that N-Si-$O_3$ is the dominant oxinitride. It is important to note that subnitride components were not observed in any spectra. If these components had been present, additional peaks would have been observed on the spectra between the Si-$Si_4$ and the Si-$N_4$ peaks.[15] When the escape angle is increased, the probed region under the interface diminishes and any subnitride components present would represent an increasing proportion of the spectrum intensity. The fact that such peaks were not observed, even at higher escape angles, is therefore significant. Since peaks can be observed when their intensity is about one percent of the total intensity, it can be concluded that less than 1% of the observed peaks are hybrids of Si bonded to one, two, or three N atoms and the complementary Si atoms. In XPS, about 10–15 atomic layers are probed at any one time. Hence, if less than 1% of the bonds are hybrids, then the interface is atomically abrupt.

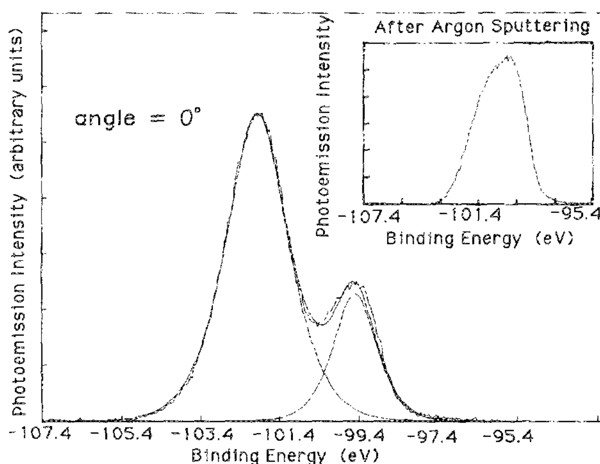


FIG. 2. Typical XPS spectrum at $\alpha = 0°$ showing the peaks associated with Si bonded to four Si atoms ($-99.5$ eV) and Si bonded to four N atoms ($-101.9$ eV). The two fitted peaks (shown by the continuous lines) are added together to reproduce the envelope spectrum shown by the continuous line through the spectrum. The inset shows the spectrum obtained after $Ar^+$ sputtering. The Si-Si peak is still present in this spectrum but subnitride components are now clearly present between it and the Si-N peak thus indicating that the interface has been destroyed.

Argon sputtering of the sample completely destroyed the $a$-Si$N_x$:H/$a$-Si:H interface as can be seen on the inset of Fig. 2. Note that the Si-$Si_4$ and the Si-$N_4$ peaks are no longer resolved in the broad featureless peak. This can be explained by the fact that nitrogen is sputtered preferentially and forms subnitride components around the interface.[16] This is also consistent with the fact that the interface is abrupt since hybrid bonds are then dominant over the probed region.

The spectra of Fig. 1 display the variation in the relative peak intensities as a function of $\alpha$. The peak heights have been normalized to bring out the differences and charge effects have been accounted for by comparing the peak binding energy with the binding energy of the carbon peak and shifting their positions accordingly. XPS studies as a function of angle $\alpha$ allow for the determination of the thickness of a thin uniform overlayer.[17,18] This thickness is determined from the relative intensities of the substrate and overlayer peaks, obtained from the fits to the spectra, by fitting with an appropriate theoretical model.

Let $I_s$ and $I_o$ be the intensities of the substrate and overlayer peaks, respectively. Then, if we assume the escape lengths to be the same in $a$-Si$N_x$:H and $a$-Si:H (these are quite close in practice) the relative intensities should be given by[17,18]

$$\frac{I_s}{I_o} = \left|\frac{I_s}{I_o}\right|_o \frac{\exp[-d/(\lambda\cos\alpha)]}{1-\exp[-d/(\lambda\cos\alpha)]}, \quad (1)$$

where $d$ is the overlayer thickness and $\lambda$ is the electron escape length. The escape length in $a$-Si$N_x$:H can be determined from the following empirical relation[19]:

$$\lambda = \frac{538}{(E_A)^2} a_A + 0.41 a_A (a_A E_A)^{1/2}, \quad (2)$$

where $E_A$ is the photoelectron energy in eV and $a_A$ the atomic radius of the molecule in nm. $a_A$ can be estimated from the density and composition of the nitride layer. Assuming a nitride composition close to $Si_3N_4$, which agrees with the composition deduced from Si-$N_4$ $2p$ and $N$ $1s$ peak intensities and corresponding atomic sensitivity factors, it was estimated that $\lambda$ was about 14 Å. Figure 3 shows the relative intensities of the Si-$Si_4$ peak (substrate) over the Si-$N_4$ peak

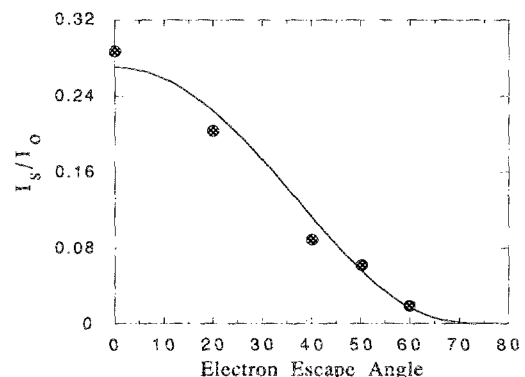


FIG. 3. Relative intensities of the peaks associated with Si bonded to four Si atoms $I_s$ over Si bonded to four N atoms $I_0$. The data points are obtained from the fits to the XPS spectra and the continuous line is the fit obtained from Eq. (1).

(overlayer) along with the fit from Eq. (1). The fit is in excellent agreement with the data and gives an overlayer thickness of 38 Å ($\pm 3$ Å) in agreement with the thickness determined from the deposition rate assuming a steady growth rate. This indicates that the peak analysis was carried out consistently.

In this letter we have shown that XPS measurements as a function of angle, obtained from a single sample, can probe the interface between *a*-$SiN_x$:H and *a*-Si:H for overlayer thicknesses typical of those frequently encountered in superlattices and quantum well structures. From the analysis we determined that subnitride peaks constitute less than 1% of the total spectrum intensity indicating that these components form much less than a monolayer. $Ar^+$ sputtering destroyed the interface and the fit of a theoretical model gave the expected overlayer thickness thus indicating that the analysis was carried out consistently. Therefore, the overall analysis supports the presence of only two peaks and we conclude that the interface is atomically abrupt.

The authors gratefully acknowledge helpful discussions with Jolanta Sapieha of Ecole Polytechnique for data analysis. This work was funded in part by the "Conseil de Recherche en Sciences Naturelles et Génie du Canada" (CRSNG).

[1]B. Abeles and T. Tiedje, Phys. Rev. Lett. **51**, 2003 (1983)
[2]B. Abeles and T. Tiedje, *Amorphous Semiconductor Superlattices*, in Vol. 21 of *Semiconductors and Semimetals*, edited by Jacques I. Pankove (Academic, New York, 1984), p. 407.
[3]J. Kakalios, H. Fritzsche, N. Ibaraki, and S. R. Ovshinsky, J. Non-Cryst. Solids **66**, 339 (1984).
[4]M. Hirose and S. Miyazaki, J. Phys. C **5**, 589 (1987).
[5]M. Tsukude, S. Akamatsu, S. Miyazaki, and M. Hirose, Jpn. J. Appl. Phys. **26**, L11 (1987).
[6]N. Ibaraki and H. Fritzsche, Phys. Rev. B **30**, 5791 (1984).
[7]S. Miyazaki, Y. Ihara, and M. Hirose, Phys. Rev. Lett. **59**, 125 (1987).
[8]H. Ugur, Phys. Rev. B **34**, 2576 (1986).
[9]M. Hirose and S. Miyazaki, J. Non-Cryst Solids **66**, 327 (1984).
[10]H. J. Trodahl, M. Forbes, D. G. A. Nelson, and A. Bittar, J. Appl. Phys. **62**, 1274 (1987).
[11]H. W. Deckman, J. H. Dunsmuir, and B. Abeles, Appl. Phys. Lett. **46**, 171 (1985)
[12]L. Yang, B. Abeles, W. Eberhardt, H. Stasieski, and D. Sondericker, Phys. Rev. B **35**, 9395 (1987)
[13]L. Yang, B. Abeles, W. Eberhardt, H. Stasieski, and D. Sondericker, Phys. Rev. B **39**, 3801 (1989).
[14]T. Bekkay, E. Sacher, and A. Yelon, Surf. Sci. **217**, L377 (1989).
[15]R. Karcher, L. Ley, and R. L. Johnson, Phys. Rev. B **30**, 1896 (1984).
[16]J. N. Chiang and D. W. Hess, J. Appl. Phys. **65**, 3430 (1989).
[17]D. Briggs and M. P. Seah, eds., *Practical Surface Analysis by Auger and x-ray Photoelectron Spectroscopy* (Wiley, New York, 1983).
[18]A. Iqbal, W. B. Jackson, C. C. Tsai, J. W. Allen, and C. W. Bates, Jr., J. Appl. Phys. **61**, 2947 (1987).
[19]M. P. Seah, Vacuum **34**, 463 (1984).

Applied Physics Letters is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see http://ojps.aip.org/aplo/aplcr.jsp
Copyright of Applied Physics Letters is the property of American Institute of Physics and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.

Applied Physics Letters is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see http://ojps.aip.org/aplo/aplcr.jsp