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Initial stages of MgO/Si and Si/MgO interface formation

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The formation of MgO/Si(111) and Si/MgO(111) interfaces was investigated by Auger-electron and photoelectron spectroscopy using synchrotron radiation. These interfaces are found to be rather abrupt. A chemically reacted buffer layer of about 1 monolayer thickness was found between bulk MgO and Si. It is concluded that the Mg–O or Si–Si bonds are not broken in the buffer layer, with no interdiffusion of the components.

1. Introduction

The formation and the properties of semiconductor interfaces involving an insulating component constitute a field of increasing interest due to applications in various fields of microelectronics [1–3]. Since the discovery of high-T_c superconductors, considerable attention has been paid to the formation of heterogeneous interfaces between insulators and high-T_c materials [4]. The procedures for preparing these interfaces have to be considered with great care, since the superconducting properties of the high-T_c materials are not supposed to change at the interface. Considering silicon/ insulator/ superconductor interfaces, the use of SiO_2 as the insulating component, in particular, is not promising due to the high temperatures required in forming this interface, which will destroy the superconducting properties of all presently known high-T_c materials. In this respect, MgO seems to be a better choice. A further advantage of this insulator lies in the possibility of using it as an oriented substrate for growing epitaxial high-T_c films [5].

The application of fast-tunneling and quasi-ballistic transport processes in high-speed electronic devices constitutes another important field involving thin insulating films [6]. MgO is known to be an appropriate substance for such applications, since its interfaces with metals and semiconductors are found to be generally rather abrupt and non-reactive [1,7], and it is further possible to grow very thin single-crystalline layers of it.

Various investigations have addressed questions of adsorption of metal films on MgO crystal faces [1,8]. In the present work, we report on a study of the formation of MgO/Si(111) and Si/MgO(111) interfaces employing Auger-electron spectroscopy (AES) as well as photoemission (PE).

2. Experimental details

The AES measurements were performed with a spectrometer equipped with a modified cylindrical-mirror analyzer that provides an energy resolution of 0.2%. The energy of the primary

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electron beam was 3 keV with an amplitude modulation of ±0.5 eV. The PE results were obtained with the 3m-TGM-4 monochromator (Toroidal Grating Monochromator) at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using a VSW-ARIES chamber. In both chambers, the base pressures during the measurements were in the low 10^{-10} Torr range.

Si(111) wafers, cleaned under UHV conditions by standard procedures, were used as silicon substrates [9]. MgO was evaporated from a $3 \times 1 \times 1$ mm^3 MgO crystal that was heated by a surrounding tungsten coil. The MgO(111) substrate was prepared by depositing at room temperature 15 Å (~3 ML) of MgO on a previously cleaned Mo(011) surface followed by annealing at ≃650°C. Quality and surface structure of the substrates were controlled by low-energy electron diffraction (LEED) and AES. The analysis of the intensities of the MgLVV and OKLL Auger lines shows that such a procedure results in thin MgO films, in which the top O-layer is thermodynamically stabilized by O-vacancies [10]. Note that the properties of these films are similar to those of a bulk MgO crystal [11]. Silicon was evaporated from a Si wafer that was heated directly by electrical-current throughput. The MgO and Si coverages were determined by a quartz microbalance.

Formation of both MgO/Si(111) and Si/MgO(111) interfaces was investigated by AES, where the SiLVV, MgLVV and OKLL Auger line intensities were monitored. Photoelectron spectra of Si2p and Mg2p core levels as well as valence band spectra were measured for the MgO/Si(111) interface system. The Si2p signals were analyzed numerically assuming Lorentzian line shapes convoluted by a Gaussian profile to account for finite lifetime and experimental resolution.

3. Experimental results

3.1. MgO / Si(111): AES results

In fig. 1a we present MgLVV and SiLVV Auger spectra for a clean Si(111) substrate and

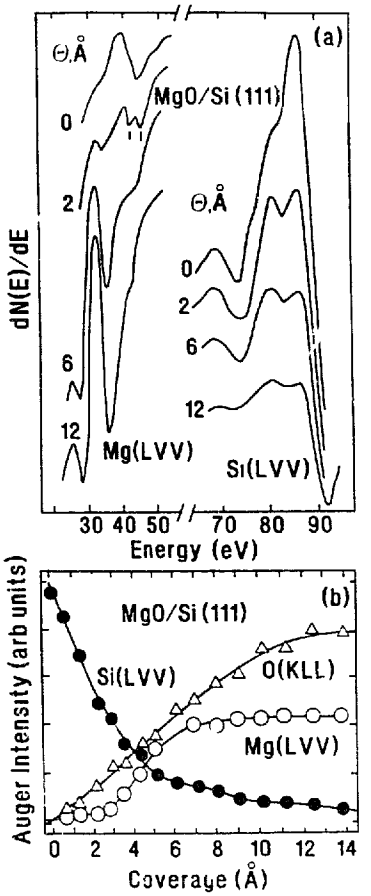

Fig 1 (a) MgLVV and SiLVV Auger spectra in $dN(E)/dE$ mode for MgO/Si(111) as a function of MgO coverage Features corresponding to Mg–Si reaction ($\Theta = 2$ Å) are marked by vertical bars (b) Peak-to-peak intensities of MgLVV, SiLVV and OKLL Auger signals as a function of MgO coverage

for Si(111) with various MgO coverages, Θ. Note that even for relatively low MgO coverages ($\Theta \approx 6$ Å), the line shape of the MgLVV emission and its energy position are similar to those of bulk MgO. Spectra in the range of submonolayer and monolayer coverages, $\Theta < 4$ Å (see spectrum for $\Theta = 2$ Å), exhibit a different behavior, with two additional structures observed at 43 and 45 eV, respectively. Despite the overlap in energy with the 45-eV feature in the spectrum of clean Si, these structures cannot be due to Si only, since other Si-derived Auger lines are not changing in a similar significant way. Following ref. [12], we assign these structures to a MgLVV AES signal from Mg interacting with Si. The superposition of these structures with the 45 eV features of Si

distorts its line shape and complicates a more profound analysis. The Si LVV AES spectra, shown for a variety of MgO coverages in fig. 1a, indicate the absence of strong Si–O interactions; this would in particular involve the formation of a SiO_2 phase. The spectra revealed only weak interactions giving rise to a splitting of the Si LVV line into two peaks. We assign the peak at lower energy (at $\simeq 83$ eV) to a SiO component [13].

Peak-to-peak intensities versus MgO coverage are shown in fig. 1b for the three Auger lines studied. The intensity of the Si LVV line exhibits a simple exponential decay with an attenuation length of ~ 3 Å, indicating the absence of Si diffusion. In the submonolayer range ($\Theta < 3$ Å), the O KLL AES line grows much faster than the corresponding Mg LVV line. For higher coverages ($\Theta \geq 3$ Å), both lines show a similar behavior, however, with the O KLL signal saturating at higher MgO coverages. This can be explained by the different sampling depths of the O KLL and Mg LVV Auger electrons due to the different kinetic energies. Upon saturation ($\Theta > 12$ Å), the ratio of intensities of the Mg LVV and O KLL Auger lines is close to that of bulk MgO. The slower increase in intensity of the Mg LVV line at low coverages as compared to that of the O KLL line suggests that in the submonolayer and monolayer range the MgO molecules are oriented with the Mg atoms attached to the Si substrate and the O atoms sticking out.

3.2. MgO / Si(111); core-level and valence-band PE results

In order to further illuminate the process of Mg–Si interaction, PE measurements of the Si 2p and Mg 2p core-levels as well as the valence-band region were performed.

Representative Si 2p core-level PE spectra of various MgO and Mg coverages on Si(111) taken at a photon energy of 125 eV, are shown in fig. 2a, including the results of least-squares fit analyses. The spectrum at the bottom of fig. 2a was obtained from a freshly cleaned Si(111)7 × 7 surface. It was fitted with two spin–orbit-split doublets (SO splitting: 0.60 ± 0.02 eV) with identical line widths, representing the bulk (b) and surface

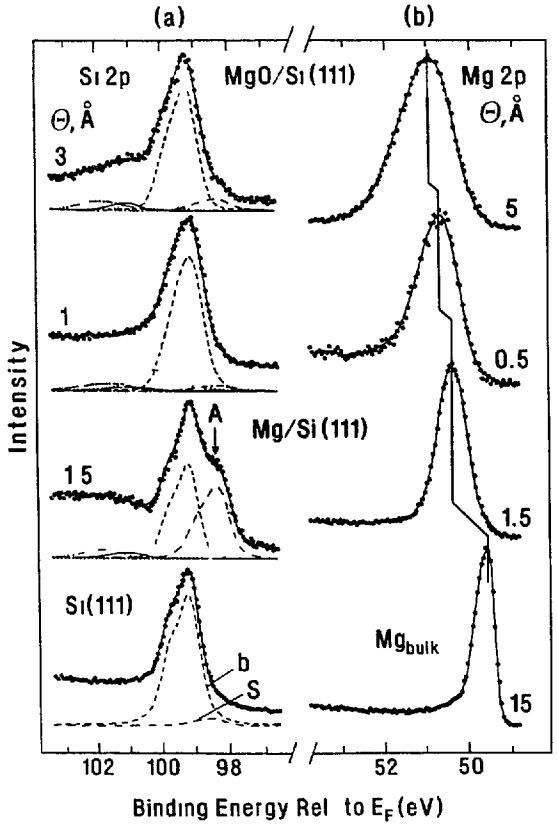

Fig 2. (a) Si 2p, $h\nu = 125$ eV and (b) Mg 2p, $h\nu = 80$ eV, core-level PE spectra of Mg/Si(111) and MgO/Si(111) The solid lines through the Si 2p data points represent the results of least-squares fit analysis. The dashed subspectra represent the non-reacted Si substrate, with surface and bulk features marked by s and b, respectively. The dash-dotted subpectra originate from the reacted buffer layer at the Mg–Si interface. In addition, three separate Si 2p signals are observed at higher binding energies and assigned to Si^+ (dotted), Si^{2+} (solid) and Si^{3+} (dash-double-dotted) species contained in the Si–O reaction products.

(s) components. The surface-core-level shift is found to be -0.80 ± 0.05 eV, and the intensity ratio between surface component and total (surface + bulk) intensity is 0.05 ± 0.01. These values are in close agreement with previous results for Si(111)7 × 7 [14].

Upon deposition of MgO, new structures appear both at the left and the right side of the bulk Si component (dashed line). Following Himpsel et al. [14], the high-binding energy parts of the spectra for $\Theta = 1$ and 3 Å were fitted by additional doublets corresponding to Si^+ (dotted line), Si^{2+} (solid line) and Si^{3+} (dash-double-dotted line) core-level signals from Si atoms with differ-

ent oxidation states. The absence of a Si^{4+} signal (SiO_2 phase) and the relatively low intensities of the Si^{+}, Si^{2+} and Si^{3+} signals indicate a weak Si–O interaction.

In order to identify the low-binding energy structure in the spectrum of MgO/Si, we have additionally studied the Mg/Si(111) interface. Fig. 2a shows the spectrum corresponding to a low Mg coverage ($\Theta = 1.5$ Å). The shoulder (A) can be fitted by an additional doublet shifted by 0.88 eV to lower binding energies relative to the substrate-Si component. A calculation of the binding energy (BE), performed on the basis of the Miedema scheme [15], indicates that the energy of the reacted phase has a value close to that of Mg_2Si. On the other hand, polarization-dependent surface EXAFS measurements have shown that the Mg atoms are on fourfold atop (T_4) position above the second layer of Si atoms [16]. Even a mild thermal treatment leads to the desorption of most of the adsorbed Mg atoms, independent of the initial coverage. This indicate that the binding forces between Mg and Si are relatively weak.

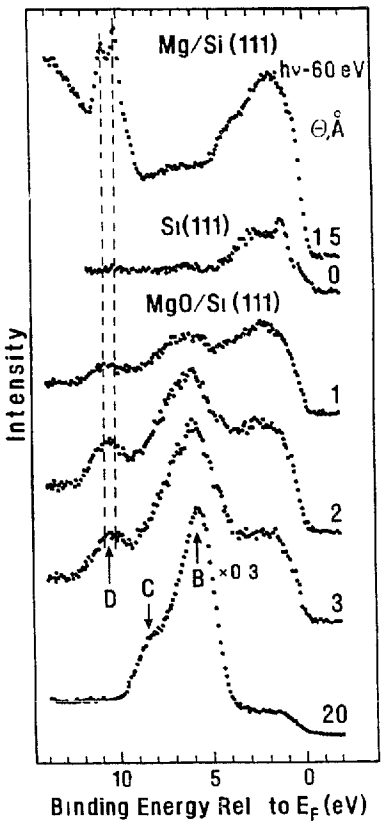

Fig 3. Valence-band PE spectra of MgO/Si(111) interfaces for various MgO coverages, for comparison, a spectrum taken from a Mg/Si(111) interface ($\Theta = 1.5$ Å) is also shown. Features typical for bulk MgO are marked by B and C. Feature D represents the Auger signal from the reacted Mg/Si interface layer

Based on these results, an additional doublet with the binding energy and width of the Mg–Si reacted component has been employed in a fit of the low-binding-energy part of the Si 2p PE spectra of the MgO/Si(111) interface. The intensity of this component grows clearly with deposition of MgO and saturates for $\Theta \approx 4$ Å, indicating again a weak Mg–Si interaction.

In contrast to the Si 2p PE spectra, the Mg 2p PE lines for MgO/Si and Mg/Si interfaces are rather structureless (fig. 2b), although they show a strong variation in line width and binding energy upon deposition of either MgO or Mg. The BE shift between the maxima of the Mg 2p line for bulk Mg and for MgO is 1.41 eV, while the difference in BE's for bulk Mg and the Mg–Si compound (Mg/Si interface, $\Theta \approx 1.5$ Å) is only 0.82 eV. The Mg 2p line of MgO/Si for low coverages ($\Theta = 0.5$ Å) shows a BE shift of 1.13 eV. This value lies between those of Mg–Si and MgO compounds indicating the presence of a Si–Mg–O-like chemical phase at the interface for low MgO coverages.

Fig. 3 displays valence-band PE spectra obtained at $h\nu = 60$ eV for Si(111) covered by MgO layers with various thicknesses. A characteristic spectrum of an Mg/Si interface is also shown for comparison. Upon deposition of MgO, the valence-band structure of the Si(111) surface vanishes and is replaced by a structure typical for bulk MgO (fig. 3, B and C). The spectrum for a high MgO coverage ($\Theta = 20$ Å) differs considerably from the spectra observed for low coverages, mainly by the absence of structure D, which is also missing in the spectrum of clean Si. The top spectrum in fig. 3 represents the valence-band PE spectrum of Mg/Si for $\Theta = 1.5$ Å. Comparing this spectrum with those observed for low coverages of MgO on Si(111), it is evident that structure D is the result of Mg–Si interactions. Furthermore, its absence in He I-excited PE spectra for both Mg and MgO [17] suggests that it origi-

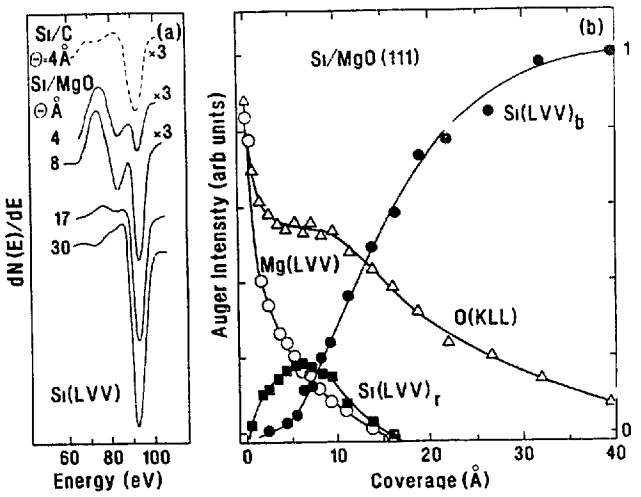

Fig. 4. (a) Si LVV Auger spectra of the Si/MgO(111) interface for various Si coverages. For comparison, a representative spectrum of the non-reactive Si/C interface is also shown (dashed line). (b) Intensity versus coverage of the Mg LVV and O KLL Auger signals as well as of the reacted (Si LVV_r) and non-reacted (Si LVV_b) components of the Si LVV Auger signal.

nates from an Auger transition with equal energy as the Mg LVV line from the Mg–Si reacted component (fig. 1a, $\Theta = 2$ Å). The calibration of the energy scales in figs. 1a and 3 was obtained by taking into account the work functions of the analyzers used in the two setups. The absence of this structure at higher coverages shows that Mg–Si interactions are confined to the submonolayer and monolayer regime.

3.3. *Si / MgO(111): AES results*

Si LVV AES spectra of the Si/MgO interface are shown in fig. 4a for various Si coverages. A characteristic spectrum of the non-reactive Si/C interface is also given in fig. 4a for comparison (dashed line). At low Si coverages, the Si LVV signal contains the structure at 83 eV mentioned in section 3.1. The absence of this structure in the spectrum obtained for a similar Si coverage on carbon suggests its origin in a reacted SiO phase (see fig. 1a). As in the case of MgO/Si, no signal from a SiO_2 phase is observed. Upon further deposition of Si, the intensity of the structure at 83 eV decreases and becomes negligible at a coverage of $\simeq 15$ Å. For higher Si coverages, the Si LVV spectra reveal a line shape typical for bulk Si.

The analysis of Auger intensities reveals a simple exponential decay for the Mg LVV signal, with a mean sampling depth of $\simeq 4$ Å (fig. 4b). In contrast to the MgO/Si interface, almost no changes in line shape of the Mg LVV spectra are observed for different coverages of MgO.

The O KLL Auger intensity decreases with increasing Si coverage, showing a shoulder in the region where the signal from the reacted SiO phase is present (fig. 4b, Si LVV_r curve). In this region, the signal from non-reacted Si has a very low intensity (Si LVV_b curve).

4. Discussion

From the experimental results it is obvious that the MgO/Si(111) and Si/MgO(111) interfaces exhibit rather similar properties. Formation of the MgO/Si(111) interface leads to Mg–Si reactions only in the submonolayer and monolayer coverage range (figs. 1a, 2a and 3). For these coverages, only a weak Si–O interaction is observed (figs. 1a and 2a). These findings lead us to conclude that in the first MgO monolayer deposited on Si(111) the MgO molecules are oriented with the Mg atoms towards the Si(111) substrate. This assumption is supported by the coverage dependence of the Mg LVV Auger intensity (fig. 1b), which exhibits a jump at a coverage of $\simeq 3.5$ Å. After the first double layer is completed, the MgO molecules seem to rearrange themselves in a way similar to the CaF_2/Si system [18]. This process leads to the formation of a MgO/Si(111) interface structure consisting of a thin buffer layer at the interface, which is characterized by complex Si–Mg–O chemical bonds. The thickness of this buffer layer is estimated to be close to 1 monolayer.

On the other hand, the Si/MgO(111) interface exhibits weak Mg–Si interactions, but rather intense Si–O interactions. For low coverages, the Si atoms occupy vacancy positions in the upper O layer (see section 2) or are deposited on top of it. In both cases, the Si–O interaction results in a

rearrangement of the O atoms. The shoulder in the plot of the O KLL Auger intensity versus Si coverage (fig. 4b) reveals that the O atoms are moved away slightly from the substrate under the influence of the Si atoms. This process is only observed for Si coverages in the region of 1–2 ML, and it does not lead to Mg–O bond breaking, since no metallic Mg features are observed.

The simple exponential damping of the substrate signal in both interfaces, with a relatively small attenuation length of $\simeq 3$–4 Å, signals abrupt interfaces as well as the absence of interdiffusion. Chemical bonding between the two nonreacted MgO and Si materials will only play a role in the thin interfacial region. We conclude from the present study of the properties of these interfaces that MgO is indeed a promising candidate for the applications mentioned in the introductory section.

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References

[1] G. Raatz and J Woltersdorf, Phys Status Solidi (a) 113 (1989) 131
[2] H. Onishi, C. Egawa and T. Aruga, Surf Sci. 191 (1987) 479.
[3] C.R. Henry and H. Poopa, J. Vac. Sci. Technol. A 6 (1988) 1113.
[4] W.T. Lin, H.C. Chu, Y.L Chu, H S. Lin, Y.K. Fang, C.Y. Chang, P.T Wu and J.H. Kung, Thin Solid Films 185 (1990) 159.
[5] F. Sumiyoshi, K. Uehigashi, H. Yamaguchi, Y. Hakuraki, H Shimura and S Miyahara, Appl. Phys. Lett. 58 (1991) 2297.
[6] D.C. Herbert, Semicond Sci. Technol. 3 (1988) 1129.
[7] M. Tonouchi, Y. Sakaguchi and T. Kobayashi, J. Appl. Phys. 62 (3) (1987) 961.
[8] H.J. Ou and J.M Cowley, Phys. Status Solidi (a) 107 (1988) 719.
[9] S.L. Molodtsov, C. Laubschat, G Kaindl, A M Shikin and V.K Adamchuk, Phys Rev. B 44 (1991) 8850
[10] V.K. Adamchuk, G V. Prudnikova and A.M Shikin, to be published.
[11] T T. Magkoev, G.G. Vladimirov and G.A. Rump, Poverhnost (USSR) 12 (1988) 88.
[12] A J. Bevolo and H.R Shanks, J Vac Sci Technol A 1 (1983) 574
[13] A.M. Shikin and G.V Purdnikova, to be published.
[14] F J. Himpsel, F.R. McFeely, A. Taleb-Ibrahimi and J A Yarmoff, Phys Rev B 38 (1988) 6084.
[15] A R Miedema, R Boom and F R de Boer, J Less-Common Met. 41 (1985) 283
[16] D Vandré, L Incoccia and G Kaindl, Surf Sci 225 (1990) 233
[17] J C Fuggle, Surf Sci. 69 (1977) 581
[18] D. Rieger, F J. Himpsel, U.O Karlsson, F R McFeely, J.F. Morar and J.A Yarmoff, Phys. Rev B 34 (1986) 7295.