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Surface reconstruction of α-(0001) sapphire: An AFM, XPS, AES and EELS investigation

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Single crystal α-(0001) sapphire substrates have been used widely for the growth of large band gap or ferroelectric materials such as GaN, ZnO, AlN and $LiNbO_3$ for applications in optoelectronics devices [1–4]. These substrates are found to support heteroepitaxial growth of large band gap materials besides possessing unique properties such as hardness, chemical inertness, high melting point and optical transparency. In many cases of heteroepitaxial film growth, some extent of prior surface reconstruction of the sapphire substrate is necessary. This is usually done by heating or annealing the sapphire substrate. However different types of surface could be formed by thermal treatment under atmosphere or vacuum as well as by ion sputtering. In previous surface studies the sapphire surface was usually sputtered and annealed in a UHV environment at temperatures exceeding 1000 °C, resulting in a change of structure [5–8]. Successive annealing of sapphire in vacuum transforms the so-called (1×1) into the $(3\sqrt{3} \times 3\sqrt{3})$ R30° and $(\sqrt{31} \times \sqrt{31})$ R ± 9° LEED patterns [7]. It is interesting to note that in a study on the effect of annealing by Baik *et al.* [9], the closed (0001) surface area shows the LEED pattern of the $(\sqrt{31} \times \sqrt{31})$ R ± 9° structure while the open surface area indicates no evidence of the $(3\sqrt{3} \times 3\sqrt{3})$ R ± 30° or the $(\sqrt{31} \times \sqrt{31})$ R ± 9° patterns. Here the closed surface area of the α-(0001) is created by placing two macroscopically smooth crystal surfaces together while the open area is exposed to air directly in the annealing process. Susnitzky and Carter [10] claim to obtain the $(3\sqrt{3} \times 3\sqrt{3})$ R ± 30° structure but not the $(\sqrt{31} \times \sqrt{31})$ R ± 9° reconstruction on α-(0001) thin foils that have been ion-milled and later annealed in air at 1400 °C. In addition the surface changes are accompanied by a change in the chemical composition of the surface topmost layers. There is evidence that certain surface structures are oxygen deficient or aluminum rich where the aluminum cation Al^{3+} is reduced in the topmost layers [6, 11].

The ability of the α-(0001) sapphire to undergo various changes in surface structures as well as the relative ease of oxygen evolvement and incorporation imply the need for a deeper understanding of its surface properties since surface changes can influence the growth of deposited materials. In this work we investigate the nature of surface reconstruction induced by annealing in air using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and electron energy loss spectroscopy (EELS).

Single crystal α-(0001) sapphire substrates obtained from Escete Single Crystal Technology are used in this experiment. The sapphire substrates are cleaned with acetone, methanol and ethanol. An annealing treatment is then performed to induce surface reconstruction. The substrates are annealed in air at 1400 °C for 1 h in a controlled environment tube furnace to obtain the reconstructed surface.

Surface morphology of the as-received and the reconstructed α-(0001) sapphire samples is analyzed using AFM. The AFM images are obtained in contact mode in air. The XPS wide survey measurements are performed at a pass energy of 100 eV at 1 eV steps between data points while single element and valence band scans are performed at a pass energy of 20 and 0.1 eV steps. The primary electron energies for the AES and EELS measurements are 10 and 1.5 keV respectively. The beam diameter is 100 nm while the beam current is 15 nA.

Fig. 1a shows the AFM image of the reconstructed sapphire substrate surface with distinct steps forming after being annealed for 1 h at 1400 °C in air while Fig. 1b shows the height profile taken along the line indicated in Fig. 1a. The driving force for the formation of the steps is the decrease in surface energy [12, 13]. The height profile shows that the atomic steps range from ∼0.2 to ∼3 nm. The terraces separated by these steps are atomically smooth. The sapphire lattice can be described as a hexagonal unit cell that is represented in the [0001] direction by six alternating oxygen layers, each layer being separated by a double layer of aluminum. The dimension of the unit cell in the [0001] direction is $c = 1.299$ nm. Thus an atomic step height of $c/6$ (∼0.22 nm) would correspond to the distance between neighboring oxygen layers or aluminum layers. Larger steps are believed to be formed by the bunching of the smaller $c/6$ steps.

Unlike the reconstructed α-(0001) sapphire substrate surface the as-received surface consists of irregular surface corrugations and scratches due to commercial polishing. Fig. 2 is an AFM image of the as-received sapphire surface with a calculated rms roughness value of 0.3 nm.

Surface analysis of the α-(0001) sapphire substrates is performed without argon ion etching or sputtering as this process is found to affect the nature of the sapphire surface. Fig. 3 shows the XPS Al 2p peak of the sapphire substrate that is subject to argon ion etching

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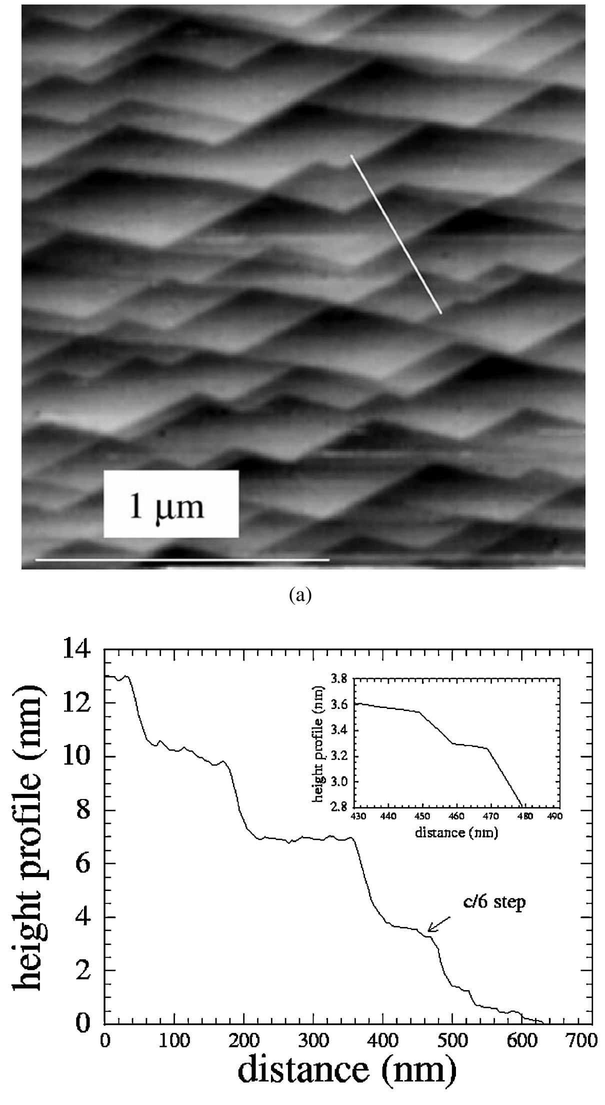

(a)

(b)

Figure 1 (a) AFM (2 μm × 2 μm) image of the reconstructed surface induced by annealing in air. (b) Height profile of the steps taken along the line shown in Fig. 1a.

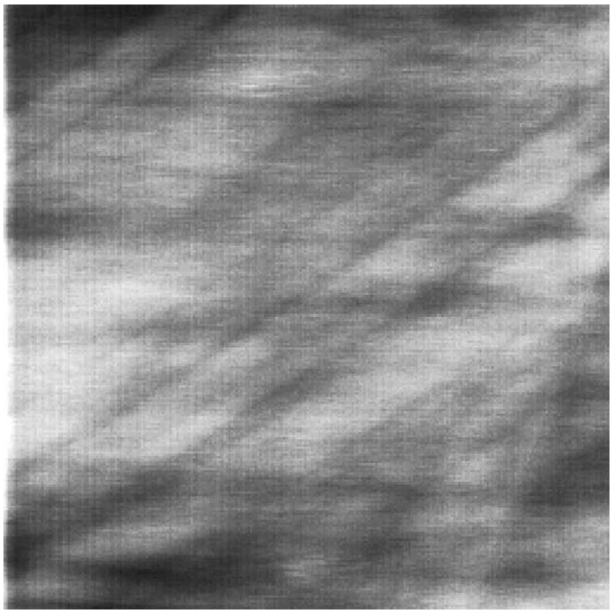

Figure 2 AFM (2 μm × 2 μm) image of the as-received sapphire surface.

for 2 min. The ion gun is operated at 3 kV and 15 mA. As a result of argon ion etching the Al 2p peak has two components at ~74.4 and ~72.6 eV, corresponding to the Al 2p peak of sapphire and the metallic state of aluminum respectively. The effect of ion sputtering or etching was also observed by Ohuchi and Kohyama [8], and Itara *et al.* [14]. When ion sputtering was performed, Ohuchi and Kohyama [8] reported a shift in the Al 2p single peak position towards lower binding energy corresponding to metallic aluminum while Itara *et al.* [14] reported oxygen removal from the surface of sapphire.

Fig. 4 shows the Al 2p peaks of the annealed and as-received sapphire substrates. The Al 2p peak positions of the as-received and annealed substrates are observed at 74.1 and 74.4 eV respectively. The FWHM values of the Al 2p peaks are ~1.5 eV. These binding energy values are within the widely accepted value of ~74 eV for the Al 2p peak of α-(0001) sapphire substrates. In particular no shift towards the Al 2p value of metallic aluminum (~72.8 eV) is observed as a result of annealing in air. This shows that the aluminum cation in the topmost layers of the annealed sample is not reduced.

In addition there is no significant change in the band width as well as the valence band edge position. The distinct valence band spectra in Fig. 5 are easily identified as those of α-Al_2O_3. The similarity of the valence bands indicates that the short range order that determines the valence band density of states is hardly affected. The two-peak upper valence band structure and the peak due to the O 2s band are present. The lower valence band is produced from the O 2s states while the upper valence band consists of two peaks, the O 2p at the valence band maximum and the oxygen-aluminum hybridization region below it. The upper valence bands calculated by Evarestove *et al.* [15] are about 12 eV wide while a width of about 6 eV is obtained by Batra [16]. The width of the lower valence band is reported to be 5.4 eV by Evarestov *et al.* [15] while Batra [16] gives a value of about 3 eV. The shape of the valence band of the annealed sapphire is similar to that of the as-received sapphire and thus excludes the possibility that the topmost layers of the reconstructed surface consist of hydroxides and oxyhydroxides of Al [17].

Furthermore the similarity of the valence band of the annealed sapphire to that of the as-received sapphire is consistent with the XPS results of French *et al.* [18] indicating no change in the valence band width or structure as a function of increasing temperature up to 1273 K. Using *ab initio* self-consistent local density calculations by the pseudofunction method, French *et al.* [18] found that the valence band width decrease due to lattice expansion is counteracted by a broadening of the valence band due to the electron-phonon interaction.

In addition, the Auger peak shapes of the Al and O in both the as-received and annealed α-(0001) sapphire substrates are similar. The signals due to the Al and O Auger electrons occurring around 1390 and 510 eV respectively are shown in Figs 6 and 7.

Fig. 8 shows the similarity of the EELS spectra of both the as-received and reconstructed sapphire surface. A broad prominent energy loss of ~24 eV

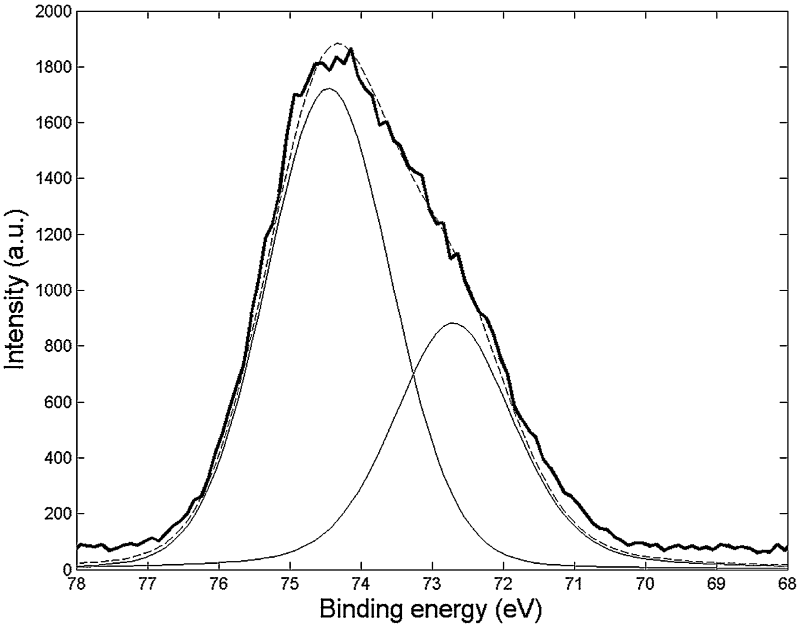

Figure 3 Al 2p peak of α-(0001) sapphire after 2 min of ion etching.

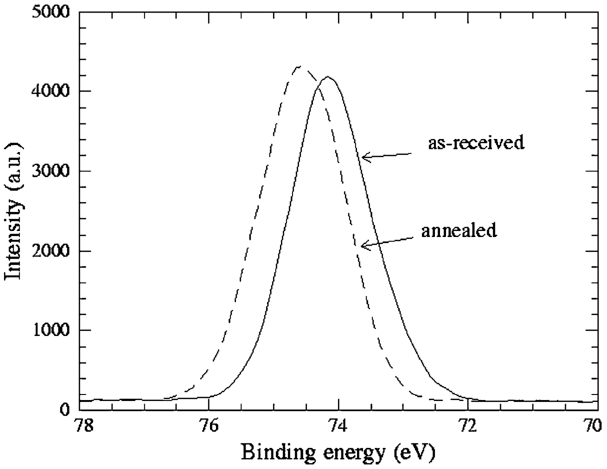

Figure 4 The XPS Al 2p peaks of the as-received and annealed α-(0001) sapphire.

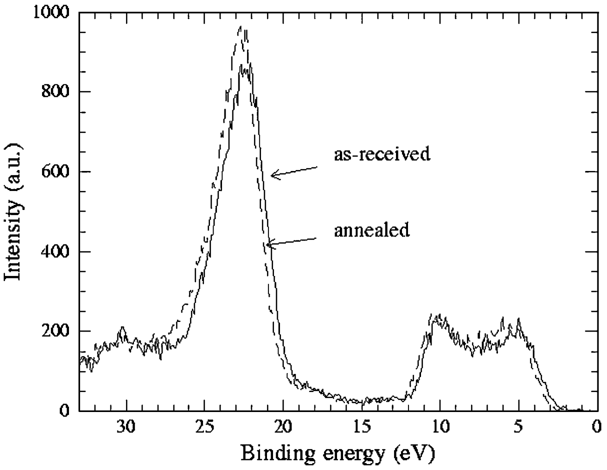

Figure 5 The valence bands of the as-received and annealed α-(0001) sapphire.

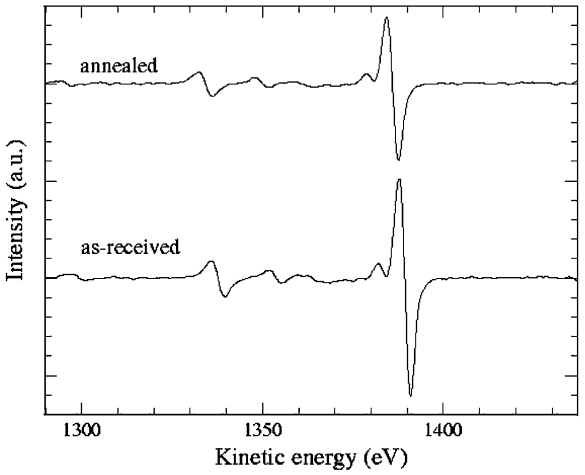

Figure 6 Comparison of the Al Auger peak shapes of the as-received and annealed α-(0001) sapphire substrates.

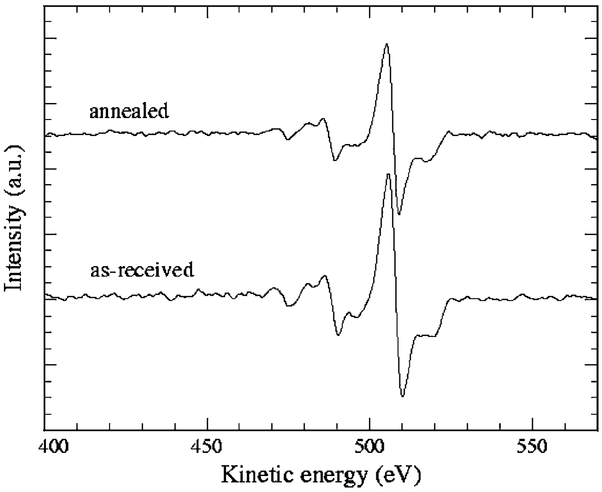

Figure 7 Comparison of the O Auger peak shapes of the as-received and annealed α-(0001) sapphire substrates.

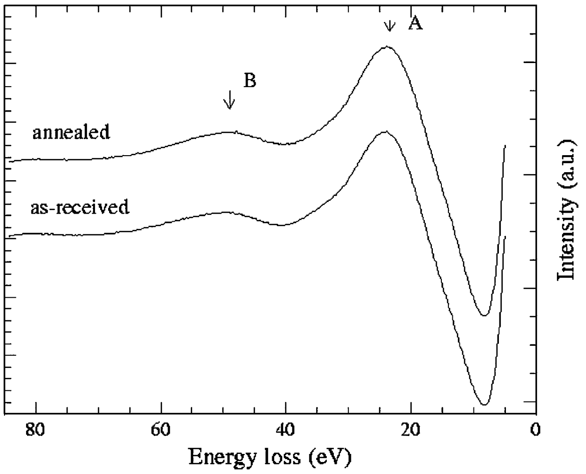

Figure 8 Comparison of the EELS spectra of the as-received and annealed α-(0001) sapphire substrates.

(feature A) is seen that is characteristic for aluminum oxide [14]. No shoulder at 15 eV energy loss that is associated with surface plasmon of aluminum is observed, implying that the surface of the sapphire substrate does not exhibit a metallic nature. The small broad peak at ~48 eV (feature B) is the two plasmon loss peak.

In conclusion it is found that the reconstructed surface of α-(0001) sapphire substrate induced by annealing in air consists of stable atomic steps ranging from ~0.2 to a few nm. The reconstructed surface also does not show a metallic nature but remains chemically stable as observed in the XPS, Auger and EELS analyses.

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