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Comparison of the electronic structures of AlN nanotips grown on p- and n-type Si substrates

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Abstract
Al and N K-edge x-ray absorption near-edge structure (XANES), scanning photoelectron microscopy (SPEM) and x-ray emission measurements were performed on AlN nanotips grown on p- and n-type Si substrates (p-AlN and n-AlN). Features and intensities in the Al and N K-edge XANES spectra of these AlN nanotips overall are similar. In contrast, the intensities of the valence-band SPEM spectra of p-AlN are apparently larger than those of n-AlN, which indicates that the valence-band density of states of p-AlN exceeds that of n-AlN. This result may be related to the observed enhancement of field-emission intensity of AlN nanotips grown on the p-type Si substrate.

1. Introduction
Aluminium nitride (AlN), a group-III nitride wide-band-gap semiconductor, is an important material for optoelectronic applications [1]. Recently, one-dimensional (1D) nanostructures of AlN have been of particular interest because they have a low turn-on field, high current...
density and a very small, even negative, electron affinity [2–4]. Electron field emission involves tunnelling of electrons from the substrate into the semiconductor materials, the transport of carriers through the materials and their emission from the surface into vacuum [5]. Accordingly, electrons injected through substrate–emitter and the emitter–vacuum interfaces strongly influence the characteristics of electron emission [6]. The properties of the emitter–vacuum interface has been extensively studied. In contrast, the substrate–emitter interface has been rarely examined. Recently, Chang et al [7] and Shi et al [8] found that wide-band-gap SiCN and AlN 1D nanomaterials had larger field-emission intensities when they were grown on the p-type Si substrate than on the n-type substrate. They explained that the direction of band bending at the p-type substrate–emitter interface-assisted field emission. Thus, the knowledge of the dependence of the conduction band, valence band and band gap of these 1D nanomaterials grown on p- and n-type semiconductor substrates is crucial in understanding the basic physics relevant to nanotechnological applications of these materials. In particular, electron-field emission from 1D nanostructured emitters concerns electron tunnelling from conduction-band, valence-band and/or surface states [9]. For this purpose, x-ray absorption near-edge structure (XANES), scanning photoelectron microscopy (SPEM) and x-ray emission spectroscopy (XES) measurements were performed to obtain the details of the electronic structures of 1D AlN nanotips grown on p- and n-type Si substrates.

2. Experiment

Al and N K-edge XANES were measured in the fluorescence mode using Dragon and high-energy spherical grating monochromator beamlines. SPEM images and spectra were acquired using the U5-undulator beamline at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. XES and corresponding XANES measurements of the N 2p states were performed at the Advanced Light Source, Lawrence Berkeley National Laboratory, beamline-7.0.1, which has a spherical grating monochromator. The quasi-aligned AlN nanotips were synthesized by a thermal chemical vapour deposition process using p- and n-type Si substrates, which were doped with boron and phosphorus, respectively. AlN nanotips grown on p- and n-type Si substrates are denoted as p-AlN and n-AlN nanotips, respectively. The details of the preparation of p- and n-AlN nanotips have been reported elsewhere [8].

3. Results and discussion

Figure 1 presents x-ray diffraction measurements of AlN nanotips and the reference thin film sample. The prominent characteristic (100), (002) and (101) peaks in figure 1 reveal that quasi-aligned AlN nanotips are polycrystalline and have a hexagonal (wurtzite) structure. Figures 1(a)–(c) display typical top-view and cross-sectional SEM images of nanotips. The AlN nanotips have average diameters of ∼10 nm at the apex and ∼100 nm at the bottom, and lengths of ∼1500 nm. They exhibit very similar morphologies. Figure 1(d) shows field-emission current densities, $J$, of p- and n-AlN nanotips as a function of the applied field obtained by Shi et al [8]. $J$ for p-AlN nanotips rises rapidly when the applied field exceeds a threshold of about 5 V µm$^{-1}$. In comparison, $J$ for n-AlN nanotips remains small. At an applied field of approximately 9 V µm$^{-1}$, $J$ for p-AlN nanotips is four orders of magnitude larger than that for n-AlN nanotips. The field emission of nanostructured SiCN exhibited a similar property [7].

Figure 2 and lower inset present the XANES spectra of AlN nanotips and the reference thin film at the Al and N K-edge, respectively. The upper inset in figure 2 shows an incident
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Figure 1. XRD measurements of quasi-aligned AlN nanotips and the reference thin film. The insets (a)–(c) display representative SEM images of the top view of p- and n-AlN nanotips and the cross-sectional view of p-AlN nanotips, respectively. The inset (d) plots field-emission characteristic curves of p- and n-AlN nanotips.

angle of $\theta = 37^\circ$ relative to the normal of the substrate. Features A$_1$ to D$_1$ (A$_2$ to D$_2$) are associated with the four features of the calculated Al (N) p-derived partial density of states (DOS) [10, 11]. These features agree well with the $\sigma$ bond (bi-layer bond) and the $\pi$ bond (c-axis bond) XANES spectra of AlN film and bulk samples obtained previously [12–14]. The variation in the general lineshapes of the Al and N K-edge XANES spectra of AlN nanotips and the reference thin film with respect to the photon energy are similar to those observed previously in the Ga and N K-edge XANES spectra of GaN nanowires and thin-film sample [15] due to the same crystal structure and similar $c/a$ ratio, where $a$ and $c$ are the wurtzite lattice constants. The general lineshapes in the Al and N K-edge XANES spectra of AlN nanotips and the thin film overall have similar features and intensities. Only the intensity of feature B$_1$ in the Al K-edge XANES spectrum of n-AlN nanotips is noticeably smaller than those in the spectra of p-AlN nanotips and the thin film.
Figure 2. Al and N (lower inset) K-edge XANES spectra of AlN nanotips and the reference thin film. The upper inset shows the incident angle $\theta$ relative to the normal of the substrate.

Figure 3 displays spatially resolved valence-band photoemission spectra of AlN nanotips and the reference film. The Al 2p SPEM images (upper insets) show the cross-sectional view of AlN nanotips and the top view of the reference film. The lower inset in figure 3 also presents the valence-band photoemission spectra from the tip region of AlN nanotips. The bright areas in the SPEM images correspond to AlN nanotips with a maximum Al 2p intensity. The spectra displayed in figure 3 are total photoelectron yields from three selected positions in the side regions of p-AlN marked by $p(s1)$, $p(s2)$ and $p(s3)$ and of n-AlN marked by $n(s1)$, $n(s2)$ and $n(s3)$, and in the surface region of the reference thin film marked by $f(1)$, $f(2)$ and $f(3)$ as shown in the upper inset. The summation over three different positions is to avoid deviations due to inhomogeneity in the samples. The zero energy refers to the Fermi level, $E_F$, which is the threshold of the emission spectra. The spectra have broad features and are dominated by N 2p–Al 2s hybridized states [13, 16]. The figure reveals that the intensities of the valence-band spectra in the sidewall regions in n-AlN nanotips are clearly smaller than
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Figure 3. Valence-band photoemission spectra of the SPEM yields from the side regions of p- and n-AlN and the reference thin film. These yields have been summed over three different positions, namely p(s1), p(s2) and p(s3) in p-AlN, n(s1), n(s2) and n(s3) in n-AlN, and f(1), f(2) and f(3) in the thin film, as shown in the upper inset, which present the Al 2p SPEM cross-sectional images of quasi-aligned AlN nanotips and the top view of the reference thin film, respectively. The lower inset presents the valence-band photoemission spectra summed over three selected tip regions p(t1), p(t2) and p(t3) in p-AlN and n(t1), n(t2) and n(t3) in n-AlN shown in the upper inset.

those in p-AlN nanotips and the thin film. The lower inset in figure 3 displays the sum of valence-band spectra contributed from p(t1)-p(t3) and n(t1)-n(t3) positions in the tip regions of p- and n-AlN nanotips, respectively, which shows that p-AlN nanotips have a larger SPEM intensity than n-AlN nanotips similar to those of sidewall regions.

As stated previously, Chang et al [7] and Shi et al [8] proposed a substrate–nanomaterial heterojunction model to explain why the electron transport across the substrate–emitter
interface yields superior electron-field emission for the p-type Si substrate than for the n-type Si substrate for wide-band-gap SiCN nanomaterials and AlN nanotips. According to this model, $E_f$ of the p-type Si substrate is slightly lower than that of the wide-band-gap 1D nanostructured SiCN/AlN, which causes holes to flow from p-type Si to SiCN/AlN to align $E_f$ (i.e. the chemical potential) on both sides. The resultant band bending at the p-type Si–SiCN/AlN interface gives rise to a ‘well’, which assists electron flow across this interface and leads to a more effective electron tunnelling into SiCN/AlN under an applied field. In contrast, a ‘barrier’ is formed at the n-type Si–SiCN/AlN interface, which hinders motion of electrons from Si to SiCN/AlN. Consequently, the nanostructured SiCN/AlN grown on the p-type Si substrate has a higher electron-emission current than that grown on the n-type Si substrate. The Al and N K-edge XANES spectra of AlN nanotips exhibit similar features and intensities, suggesting that the DOSs of the conduction band of both p- and n-AlN nanotips are similar. However, the intensities of valence-band SPEM spectra of p-AlN apparently exceed those of
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n-AlN, which suggests that the valence-band DOS of p-AlN is larger than that of n-AlN, although the measurements were performed in the absence of an applied field. This result indicates that the intensity of field-emitted electrons is strongly correlated with the valence-band DOS of AlN nanotips.

Figure 4 presents XES and corresponding XANES spectra of N 2p states of AlN nanotips and the reference AlN thin film. The N K emission spectra reflect N 2p occupied (valence-band) states and N K-edge XANES spectra reflect N 2p unoccupied (conduction-band) states of AlN nanotips and the reference film. These spectra are consistent with the results of first-principles calculations [10, 11] and the spectra of the AlN film obtained previously [12]. A well-defined band gap ($E_g$) between the valence-band maximum (VBM) and the conduction-band minimum (CBM), marked by dotted lines, is observed, as shown in figure 4. The emission and absorption spectra clearly indicate that the $E_g$ of 6.2 eV for AlN nanotips is the same as that of the reference thin film, which also agrees with earlier studies [12, 17]. The positions of the VBM and CBM are also found to be the same for p- and n-AlN nanotips and the reference thin film, which illustrates that the VBM, CBM and $E_g$ of AlN nanotips are not affected by either p- and n-type Si substrates when no field is applied.

4. Conclusion

In summary, Al and N K-edge XANES measurements for AlN nanotips grown on p- and n-type Si substrates exhibit similar features and intensities, suggesting that the DOSs of the conduction-band of both p- and n-AlN nanotips are similar. In contrast, the intensities of the valence-band SPEM spectra of p-AlN are apparently larger than those of n-AlN, which indicates that the valence-band DOS of p-AlN exceeds that of n-AlN. This result correlates with the observed enhancement of field-emission intensity of AlN nanotips grown on the p-type Si substrate.

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