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Observation of a negative electron affinity for heteroepitaxial AlN on α(6H)-SiC(0001)

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This study demonstrates the presence of a negative electron affinity (NEA) surface on AlN was grown on α(6H)-SiC. Heteroepitaxial AlN was grown on α(6H)-SiC(0001) substrates by molecular beam epitaxy techniques. The surface electronic states were characterized by ultraviolet photoemission obtained at surface normal. The observation of a sharp spectral feature at the lowest energy of the emitted electrons is an indication of a surface with a negative electron affinity. In addition, the trend of the NEA feature was examined as a function of annealing. The surface Fermi level is found to be near the middle of the AlN gap, and a possible band alignment between the AlN and SiC is presented.

The phenomenon of a negative electron affinity (NEA) occurs at a semiconductor surface when the vacuum energy level lies below the conduction-band edge. Since the bonding of common semiconductors are based on sp^3 hybridization, the valence band is derived from bonding levels and the conduction band from the antibonding atomic orbitals. Since these materials have a common bonding origin, the NEA phenomenon is more likely to occur for wide-band-gap materials. The consequence of a NEA surface is that any electrons from the valence band promoted into the conduction band can escape from the material. Possible uses for such materials include ultraviolet (UV) and x-ray detectors and cold cathode emitters. The possibility for NEA-based vacuum collector emitters also exists.[1] In this study we will examine aluminum nitride (AlN) as a candidate for obtaining a semiconducting NEA surface.

The material studied was aluminum nitride (AlN) film grown epitaxially on α(6H)-SiC(0001) substrates. Here α refers to the family of hexagonal polytypes and 6H specifies the 6 layer repeat. The (0001) surface is the Si terminated surface. Bulk crystalline AlN has a direct optical band gap of 6.2 eV and a hexagonal structure (wurtzite) and an a-axis lattice constant of 3.11 Å. In this study, the AlN growth was achieved by molecular beam epitaxy (MBE).[2,3]

The presence of a NEA can be determined by ultraviolet photoemission spectroscopy (UPS).[4–6] This technique involves directing 21.2 eV light (the He I resonance line) to the surface of the sample and detecting the spectrum of the emitted photexcited electrons as a function of electron kinetic energy. Typically, UPS is used to obtain a profile of the valence band (VB) electronic states. As such, most studies of UPS of semiconductors present data of the most energetic electrons emitted from the surface. Electrons scattered to lower energy and secondary electrons will be displayed in the spectra at lower kinetic energies. In addition, for a semiconductor which exhibits a NEA surface, a distinctive peak may be observed at the low kinetic energy (highest binding energy) end of the photoemission spectra. Shown in Fig. 1 is a schematic representation of the photoemission spectra from a semiconductor with a negative or positive electron affinity. The low kinetic energy feature is due to secondary electrons which are (quasi) thermalized at the conduction-band minimum.

The sharp features typical of a NEA have been observed from spectra of (111) and (100) diamond surfaces.[4–8] In the studies of diamond, a correlation was made between the presence of hydrogen and the NEA peak.[5,6] In addition, it was also shown that thin metal layers such as Ti or other low work function metals could induce a NEA on the diamond surface.[8,9] These measurements verify that the surface dipole can be influenced by surface processing and that the effects contribute to the observation of a NEA.

For the AlN UPS studies presented here, the SiC substrate is important for two reasons. The first is that because of the insulating character of the wide-band-gap semiconductors there could be charging problems, and the photoemission would be quickly quenched. This problem is avoided by growing a thin layer of AlN on a conducting (n-type) SiC substrate. The second benefit of the SiC substrate is the small lattice mismatch between SiC and AlN (3.11 Å vs 3.08 Å).

The AlN/SiC sample was deposited on the SiC substrate by a modified gas source MBE system.[2,3,10] The substrate was a vicinal wafer of 6H polytype (0001) (oriented 3°–4° towards $[11\bar{2}0]$) SiC which resulted in a hexagonal (2H) AlN structure. The MBE system consists of three parts: a load lock (base pressure of 5×10^{-8} Torr), a transfer tube (base pressure of 1×10^{-10} Torr), which also was used for degassing the substrates, and the growth chamber (base pressure of 5×10^{-11} Torr). Knudson effusion cells with BN crucibles and Ta wire heaters were charged with 6N pure aluminum. Ultrahigh purity nitrogen, further purified by a chemical purifier, was used as the source gas. The nitrogen gas was excited by an ECR plasma source, which was designed to fit inside the 2.25-in.-diameter tube of the source flange cryoshroud.

Prior to loading into the chamber, the SiC substrates were cleaned by a standard degreasing and RCA cleaning procedure. After undergoing a degassing procedure in ultrahigh vacuum (UHV) (700 °C for 30 min), the substrates were transferred into the deposition chamber. Epitaxial AlN films were deposited with the following conditions: nitrogen pressure: 2×10^{-4} Torr, microwave power: 50 W, aluminum cell

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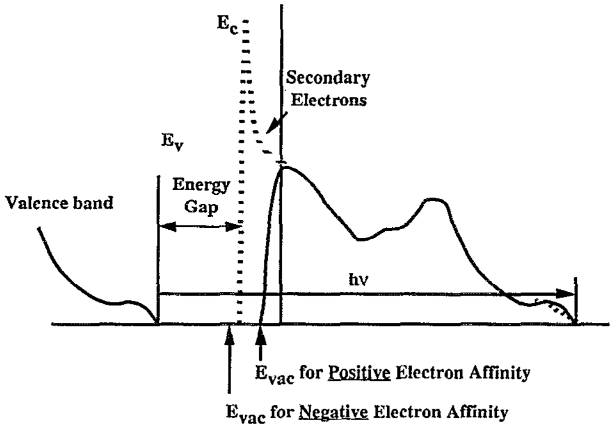

FIG. 1. A schematic of the difference in the photoemission spectra of a semiconductor with a positive or negative electron affinity.

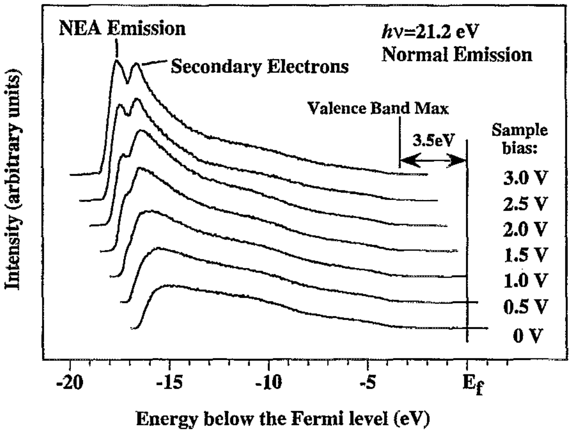

FIG. 2. The UV photoemission of AlN on 6H-SiC. The spectra were obtained at different sample bias to overcome the work function of the electron analyzer.

temperature: 1120 °C, substrate temperature: 1100 °C, deposition rate: 1000 Å/h.[2,3]

The sample was transported in air to the surface analysis system. The analysis system is made up of several chambers linked by a linear UHV transfer line. The details of the system are described elsewhere.[6,8] Among the capabilities available are UPS, low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), hydrogen and argon plasma cleaning.

The UPS chamber has a base pressure of 2×10^{-10} Torr. Operating conditions involve pressures up to 1×10^{-9} Torr, but the higher pressure is due to the helium inflow and does not contaminate the sample. The UPS system utilizes a helium resonance lamp (the He I line) to provide a source of 21.2 eV light. Photoemitted electrons are measured with a 50 mm mean radius hemispherical electron analyzer operated at a 0.15 eV energy resolution and a 2° angular resolution. The analyzer (VSW HA50) is mounted on a double goniometer and can be tilted with respect to the sample in two independent directions. The AlN/SiC samples were fastened with tantalum wire to a molybdenum sample holder. The sample holder can be biased by up to 4 V to allow low energy electrons to overcome the work function of the analyzer. The Fermi level of the system (sample and analyzer) is determined by UPS measurement of the sample holder with no sample bias (i.e., grounded). The sample holder can be heated to 1150 °C.

The UPS measurements carried out on the AlN/SiC sample as loaded are displayed in Fig. 2. The spectra were obtained with different sample bias to overcome the work function of the analyzer. In the figure, all spectra have been displaced by the applied bias so that the Fermi level aligns. Two aspects indicate the presence of the NEA. The first is the detection of a low energy peak clearly observable with a sample bias of 3.0 V, with onset occurring at a bias of 1.5 V. The two low energy peaks roughly the same height present at the 3.0 V bias are attributed to the normal secondary emission typical of UPS while the low energy feature is attributed to electrons thermalized to the conduction-band minimum. This second peak is considered as the NEA peak since the electron count drops off so quickly. The large (~3 V) bias is needed because the work function of the AlN is apparently less than that of the analyzer. The analyzer work function is between 4 and 5 eV.

The second indication of the NEA is that the width of the photoemission spectra are consistent with the model described in Fig. 1. Here the width $W=h\nu-E_g$, where W extends from the low energy limit to the valence band maximum. We have used this relation to determine the position of the valence-band maximum in the spectrum obtained with a 3 V bias. The low energy limit was determined by linear extrapolation of the back edge to zero intensity. Then using the band gap of AlN as 6.2 eV and the 21.2 eV photon energy, the valence-band maximum should then occur at 15.0 eV above this limit. The vertical line labeled VBM was obtained in this way. As is evident from the spectra, the valence-band emission extends to this energy. We also note that the results indirectly verify that the band gap of the AlN film is the same as the bulk value of 6.2 eV.

The effect of annealing in vacuum was explored. After the annealing the photoemission spectra showed a decrease in the relative intensity of the NEA related peak (Fig. 3). The AES of the as-loaded surface showed oxygen and carbon contaminates in addition to the Al and N signals. After an anneal of 700 °C the AES showed a small reduction of the oxygen and a similar scale increase in the surface carbon, a trend that continued with the 1000 °C anneal. A LEED pattern was not visible from the sample as loaded or after the anneals of 700 and 1000 °C. We note that after a short H-plasma clean a faint 1×1 pattern was visible with an electron beam energy of 80 eV and the C signal was removed. The lack of a LEED pattern for the as-loaded and the annealed samples is possibly related to the carbon and oxygen on the surface. The reduction of the NEA related features indicates that the effect is related to the surface structure and termination of the AlN.

In comparison to the UPS spectra obtained from diamond surfaces which exhibit a NEA,[3–8] the feature in diamond is significantly sharper than that observed here for the AlN. Possible causes that could contribute to a broader sig-

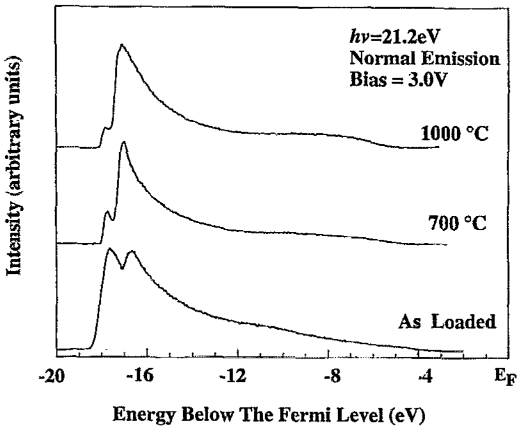

FIG. 3. The UV photoemission spectra of AlN on 6H-SiC as-loaded and after vacuum annealing at the indicated temperatures. All spectra were obtained with a sample bias of 3.0 V.

nature may be related to a more disordered surface or to the intrinsic properties of the AlN (e.g., direct band gap).

The last point that we address is the position of the Fermi level in the AlN. From Fig. 1, it is evident that the surface Fermi level occurs at ~3.5 eV above the valence-band maximum. This is near the center of the 6.2 eV band gap. From this data we suggest a possible band alignment of AlN and SiC. Here we have assumed that there is no band bending in the AlN or in the SiC near the interface. Because of the wide band gap of the AlN, it seems unlikely that there is significant band bending in the thin film. The bulk Fermi level of the SiC has been determined from the doping level of the substrates to be ~0.3 eV below the SiC conduction-band edge.[10] The results are summarized in Fig. 4. The band offsets are −0.8 eV at the valence band and 2.4 eV at the conduction band. The largest uncertainty in this proposed band offset is the band bending in the SiC. Such band bending would result in an increase in the magnitude of the valence-band offset and a decrease in the conduction-band offset. While we are not aware of any calculations of the heterojunction band offsets of wurtzite AlN on 6H-SiC, there has been a calculation of the offsets of the (110) interfaces of cubic AlN/SiC.[11] The theoretical results also indicate a type I offset with band discontinuities of 1.5 eV at the valence band and −1.2 eV at the conduction band. This is qualitatively similar to the results presented in Fig. 4.

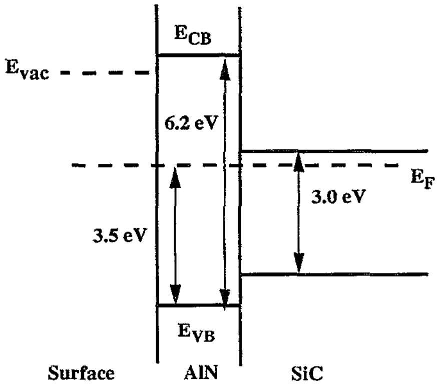

FIG. 4. A schematic of the possible band alignment of AlN on 6H-SiC.

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