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Negative electron affinity surfaces of aluminum nitride and diamond

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Abstract

The electron affinity of diamond and AlGaN surfaces are studied by UV photoemission spectroscopy. It is shown that H terminated diamond surfaces exhibit a negative electron affinity while oxide terminated surfaces exhibit a positive electron affinity. In addition, thin metal layers can also induce a NEA on both (100) and (111) surfaces of diamond. Photoemission results of AlGaN alloy films grown on 6H-SiC indicate a negative electron affinity for as-prepared and air exposed surfaces with high Al concentrations.

Keywords: Electron affinity; Nitrides; Electron emission; Surfaces

1. Introduction

Wide bandgap semiconductors have the potential of exhibiting a negative electron affinity (NEA). These materials could be key elements of cold cathode electron emitters which could be used in applications that include flat panel displays, high frequency amplifiers, and vacuum microelectronics. The surface conditions are shown to be of critical importance in obtaining a negative electron affinity. In this article, angle resolved UV-photoemission spectroscopy (ARUPS) is used to explore the effect for diamond and AlGaN surfaces. The value of UV photoemission in characterizing electron emission is that the technique emphasizes effects of the emission process. To fully characterize electron emission properties it is necessary to also employ additional measurements such as distance dependence of field emission, and secondary electron emission. These measurements have recently been compared for properties of CVD diamond films.[1]

The electron affinity of a semiconductor is defined as the energy required to remove an electron from the conduction band minimum to a distance macroscopically far from the semiconductor (i.e. away from image charge effects.). At the surface this energy can be shown schematically as the difference between the vacuum level and the conduction band minimum. The electron affinity is not, in general, dependent on the Fermi level of the semiconductor. Thus while doping can change the Fermi level in the semiconductor and the work function will change accordingly, the electron affinity is unaffected by these changes. An alternative view is that the electron affinity is a measure of the heterojunction band offset between the vacuum and a semiconductor of interest. For most semiconductors, the conduction band minimum is below the vacuum level and electrons in the conduction band are bound to the semiconductor by an energy equal to the electron affinity. In some cases, surface conditions can be obtained in which the conduction band minimum is above the vacuum level. In that case the first conduction electron would not be bound to the sample but could escape with a kinetic energy equal to the difference in energy of the conduction band minimum and the vacuum level. This situation is termed a negative electron affinity. (Note that the electron is still bound to the vicinity of the sample by coulomb forces.)

The electron affinity or work function of a material is usually ascribed to two aspects of the material (1) the origin of the atomic levels, and (2) the surface dipole due to the surface termination.[2] These effects are shown schematically in Fig.1. The atomic levels are more or less intrinsic to a material and cannot be changed. This is not the case for the surface dipole. The surface dipole can be substantially affected by surface reconstructions and surface adsorbates. As a simple example to illustrate the magnitude of this effect consider a surface with hydrogen termination, and assume that the average nuclear and electronic charges are point charges separated by 0.5 Å. Then for a surface density of $1 \times 10^{15} cm^{-2}$ we would find a 9eV effect due to the surface dipole. (Certainly complete charge transfer is

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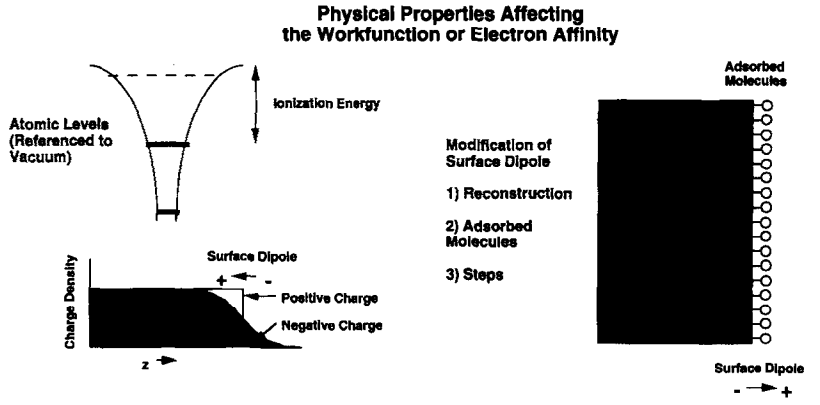

Fig. 1. A representation of the effects which contribute to the work function (or electron affinity) of any material. While the atomic levels are an intrinsic property of the material, changes in the surface bonding can substantially affect the workfunction or electron affinity.

never a reasonable possibility, but this simple calculation demonstrates the significance of the surface dipole.) Because of the large effect of the surface dipole, it is essentially impossible to determine if a material is intrinsically NEA. Thus the surface termination is critical in describing the electron affinity (or NEA) properties of a material.

One method to measure the electron affinity of a semiconductor is UV-photoemission.[3,4] The changes in the spectra due to NEA are indicated in Fig. 2. [5] The electrons from the valence band are excited into the conduction band. In transiting towards the surface, electron scattering occurs and a large number of secondary electrons accumulate at the valence band minimum. For materials with a positive electron affinity these electrons cannot escape, while for a NEA the electrons can be emitted directly and will be observed with a low kinetic energy. Thus the two effects which signify a NEA are an extension of the spectral range to lower energy and the appearance of a sharp peak at low kinetic energy. This feature will appear at the largest (negative) binding energy in typical presentations of UPS spectra.

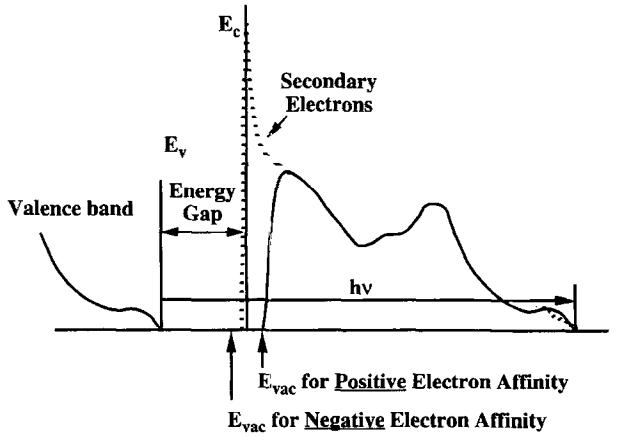

Fig. 2. A schematic of how NEA affects the photoemission spectra. For a NEA surface the spectra is broadened to lower kinetic energy and a peak due to quasi thermalized electrons is also detected at the lowest kinetic energy.

In addition to the sharp feature that is often evident in the spectra of a NEA semiconductor, the width of the photoemission spectrum (W) can be related to the electron affinity. The spectral width is obtained from a linear extrapolation of the emission onset edge to zero intensity at both the low kinetic energy cutoff and at the high kinetic energy end (reflecting the valence band maximum). From Fig. 2. it is evident that we can write the following relations:

$$\chi = h\nu - E_g - W \text{ for a positive electron affinity}$$

$$0 = h\nu - E_g - W \text{ for a negative electron affinity}$$

where E_g is the bandgap and $h\nu$ is the excitation energy. We stress that the photoemission measurements cannot be used to determine the energy position of the electron affinity for the NEA surface. Careful measurements of the width of the spectra are helpful in distinguishing whether the effect is direct emission of the electrons from conduction band states or whether excitons are involved in the emission process. The effects of excitons have recently been reported by Pate and co-workers.[6]

In addition to measurement of the electron affinity, the position of the surface Fermi level can be obtained. For a grounded sample, the Fermi level of the sample will be the same as that of the metal holder. The Fermi level of the metal can easily be determined, and the energy difference of the valence band maximum and the metal Fermi level gives the position of the surface Fermi level of the semiconductor.

2. Experimental

The experiments described in this summary article were carried out in an integrated UHV system with surface preparation, film growth and surface charac-

terization capabilities. The system consists of eight chambers interconnected by a linear sample transfer mechanism. The overall length of the sample transfer chamber is almost 35ft. A portion of the system is shown schematically in Fig. 3. This figure shows the relations of the UV photoemission system, the plasma surface processing system, the LEED/Auger systems, and the MBE chamber. In the experiments described here, the UV-photoemission measurements were made with HeI (21.21eV) radiation and the electrons were analyzed with a VSW HAC50 50mm mean radius hemispherical electron analyzer. The spectra were collected at normal emission with a collection angle of approx. 2°. The sample was biased with between 1 and 3V so that the low energy electrons can overcome the work function of the analyzer. While higher sample bias can be employed, the low bias used here is to minimize spectral distortions that occur due to changes in the effective collection angle for the higher sample bias.

In the studies of diamond, H plasma, Ar plasma exposures and anneals in UHV have been employed to process the diamond (100) and (111) surfaces. Following each surface preparation step the surfaces were characterized with UPS, LEED and AES. The effects of metals on the surfaces were also considered. In these measurements thin layers of Ni, Ti, Cu and Co have been deposited on diamond (100) and (111) surfaces. The metals were deposited on substrates terminated by oxygen, hydrogen or free of adsorbates. The Schottky barrier height can be measured by means of UPS. For a p-type semiconductor the Schottky barrier height is determined by the difference between the valence band edge and the Fermi level. For metal film thicknesses less than or equal to the electron mean free path (5) both the Fermi level of the metal as well as the valence band edge of the diamond can be observed by photoemission spectroscopy.

To avoid charging and to obtain high quality epitaxy, the AlGaN films were grown on (0001) 6H-SiC substrates. The substrates were supplied by Cree Research, Inc. [1] The SiC wafers were n-type with doping concentrations of 10^{16} to $10^{18}/cm^3$. The AlGaN alloy samples were grown by CVD (OMVPE) in a remote location and transported in ambient to the analysis system. Clean, as-grown surfaces of AlN and GaN were prepared in the integrated UHV transfer system (described above) by gas source molecular beam epitaxy (GSMBE), and transferred directly to the UPS system. The Al concentration of the alloy samples was estimated from respective cathodoluminescence measurements.

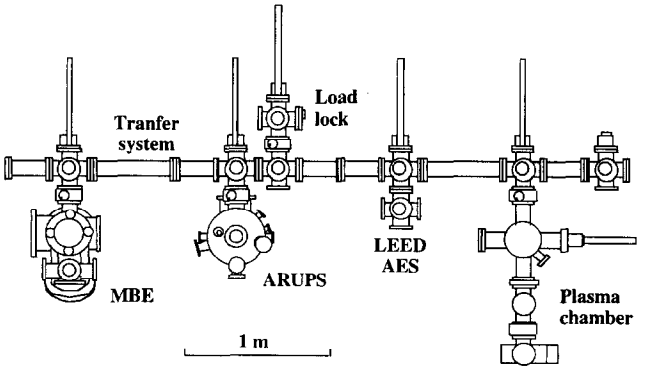

Fig. 3. A schematic of a portion of the integrated surface processing and characterization system used in the studies described here.

3. Electron affinity of diamond surfaces

As-loaded diamond (100) samples exhibit oxygen surface contaminants as evidenced by AES and a 1 × 1 unreconstructed LEED pattern, and a positive electron affinity is observed by photoemission spectroscopy. Following a 900 °C–1050 °C anneal in UHV, the oxygen is removed from the surface. The annealing temperatures vary depending on the chemical pretreatment of the diamond samples prior to loading into UHV [7 – 10]. The oxygen is removed at 900 °C for samples cleaned by an electrochemical etch and at 1050 °C for those treated with a chromic acid clean. However in both cases the removal of oxygen from the diamond (100) surface coincides with a 2 × 1 reconstructed LEED pattern and with the appearance of a sharp low-energy peak indicative of a NEA in the UPS spectra. This feature is positioned 15.7eV below the energy of the valence band maximum in the spectrum. This value corresponds to the width of a spectrum from a NEA diamond surface (i.e. 0=21.2eV–5.5eV–15.7eV). Subsequent to a hydrogen plasma exposure the intensity of the NEA peak is found to be doubled. And upon heating the samples to 1150 °C the UPS spectra are indicative of a positive electron affinity. However the NEA can be induced again by another H plasma exposure. Following both the H plasma cleans and the 1150 °C anneal the surface remained 2 × 1 reconstructed and the AES spectra did not change. It is suggested that a H plasma clean results in a uniform monohydride-terminated surface. From the intensity differences of the NEA emission it is estimated that approximately half the surface is covered by a monohydride subsequent to an anneal at the lowest temperature when oxygen is no longer observable by AES. A 1150 °C anneal is thought to remove the hydrogen from the surface leading to a positive electron affinity. In addition ab initio calculations for the 2 × 1 reconstructed surface suggest a NEA for the monohydride-terminated surface and a positive electron affinity for the clean surface [8].

Similarly a NEA can be induced on the diamond (111) surface by employing a H plasma [11]. The NEA can be removed from the surface either by means of an anneal to 950 °C or alternatively by an Ar plasma exposure. A second exposure to a H plasma leads to a

NEA again. The NEA is associated with a hydrogen terminated surface. Whereas the 950 °C anneal and the Ar plasma clean remove the hydrogen from the surface. Either one of these processes leads to a clean surface which exhibits a positive electron affinity. A number of UPS spectra on both diamond (100) and (111) surfaces are shown in Fig. 4.

The first demonstration of a negative electron affinity of semiconductors was most likely Cs coated GaAs. Here we consider the effects of metals deposited on diamond substrates. A Schottky barrier of $\Phi_B = 0.5$ eV and a metal induced NEA are determined for Ni on the clean diamond (111) face. However depositing Ni on a monohydride terminated (111) surface leads to a value of $\Phi_B = 1.0$ eV and a positive electron affinity [12]. For Ti on the adsorbate free diamond (111) face, a Schottky barrier of 1.0 eV and a NEA are obtained [13]. Similarly Cu grown on the clean C(100) surface results in $\Phi_B = 1.0$ eV and a NEA [7]. For Co deposited on the clean C(100) surface a Schottky barrier of 0.35 eV and a NEA are obtained. In contrast, for Co on the oxygen terminated C(100) face, $\Phi_B = 1.45$ eV and a positive electron affinity is found. Results from photoemission measurements of metals on diamond are summarized in Fig. 5.

Erwin and Pickett [14–17] and Pickett, Pederson and Erwin [18] performed theoretical studies of the Ni-diamond interface. A Schottky barrier height of less than 0.1 eV was calculated for the most stable configurations on the clean diamond (100) and (111) surfaces. For copper on diamond (111) surfaces the Schottky barrier height was calculated depending on the interface structure by Lambrecht [19]. A Schottky barrier of less than 0.1 eV was determined for the adsorbate free surface and ≥ 1.0 eV for the hydrogen terminated surface.

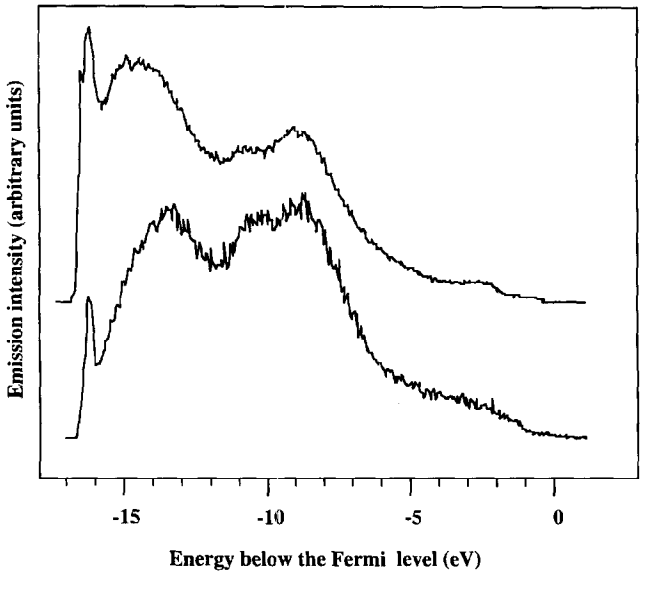

Fig. 4 UV photoemission spectra of monohydride terminated diamond (100) and (111) surface. Both surfaces exhibit a NEA.

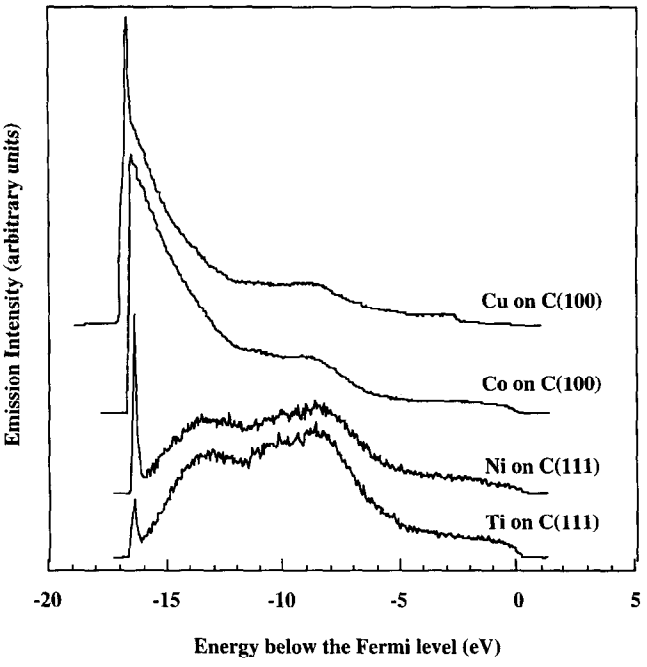

Fig. 5. UV Photoemission spectra of metals on clean diamond (100) and (111) surfaces. A low energy peak indicative of a metal induced NEA is observed for all cases shown.

Similar values for both Ni and Cu on clean surfaces are obtained. And these results indicate that the Schottky barrier depends on the interface termination.

From the results on Ni and Co it can be concluded that the Schottky barrier height for metals deposited on clean diamond surfaces is less than that for surfaces terminated by hydrogen or oxygen. Metal-diamond interfaces with a lower Schottky barrier also exhibit a lower electron affinity. Indeed, surface preparation can significantly affect the Schottky barrier height and the electron affinity for metals on diamond.

4. Electron affinity of AlGaN surfaces

The UV photoemission spectra of AlN, GaN and the two alloy samples are shown in Fig. 6. [20,21] Samples were biased with 2–3 V to overcome the work function of the analyzer, and all spectra were shifted to be aligned at the valence band maximum. The spectra were scaled such that the strongest emission was the same for all curves.

The first aspect to be noted is that the spectra of the Al rich alloy and AlN exhibit sharp strong features at the highest binding energy, which corresponds to the lowest kinetic energy. These features are often indicative of a negative electron affinity. As noted in the introduction, the feature is attributed to emission from electrons quasi-thermalized to the conduction band minimum. The emission from the $Al_{0.13}Ga_{0.87}N$ sample is signifi-

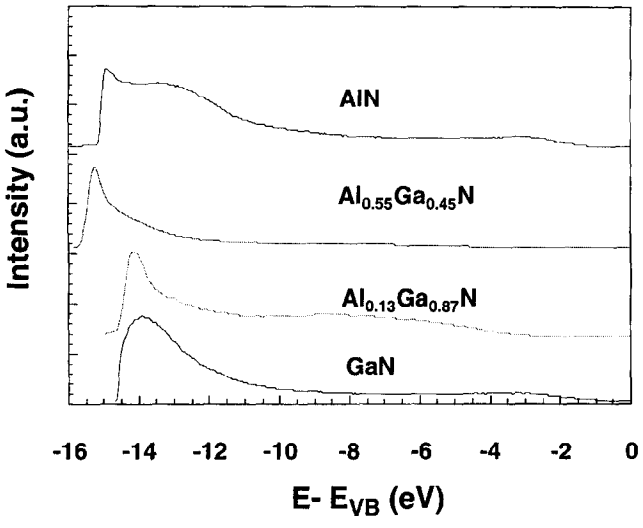

Fig. 6. The UV photoemission spectra of $Al_xGa_{1-x}N$ films grown on 6H-SiC.

cantly weaker, and the GaN emission does not show the sharp peak at all.

A second indication of the change in electron affinity with alloy concentration is the extension of the $Al_xGa_{1-x}N$ spectra to lower energy as x is decreased. A more precise description of the relation of the NEA is obtained from the spectral width. To determine the energy position of the valence band maximum, each spectrum was magnified, and the intensity was extrapolated to 0 emission. The spectral widths obtained from the $Al_xGa_{1-x}N$ samples were 14.5, 14.5, 15.5, and 15 eV for $x=0$, 0.13, 0.55, and 1.0, respectively. To apply the relations noted above, the bandgap of each sample must also be known. The reported values of the AlN and GaN bandgaps are 6.2 and 3.4 eV respectively. The band gap of the alloy samples was determined from the respective cathodoluminescence measurement. Using the relations described above, the AlN satisfies the relations for a NEA, while the $Al_{0.55}Ga_{0.25}N$ surface exhibits a low but positive electron affinity. The GaN and $Al_{0.13}Ga_{0.87}N$ surfaces, do not satisfy the relations for a NEA. We can, however, determine the value of the electron affinity of these materials and find that $\chi=$ 3.3 eV and 2.9 eV for $x=0$ and 0.13 respectively.

Another aspect that is evident from the photoemission spectra is the position of the surface Fermi level relative to the valence band maximum. It was found that E_F ranges from 2 to 3.5 eV above the valence band maximum for each sample. For the GaN and $Al_{0.13}Ga_{0.87}N$ surfaces, these values position E_F in the upper part of the gap while for the Al rich samples, the values indicate that the surface Fermi level is pinned near midgap. The surface Fermi level position and the bandgap of the alloys are indicated in Fig.7. The pinning at midgap may be an indication of surface states or increased impurity incorporation. In particular, the strong affinity

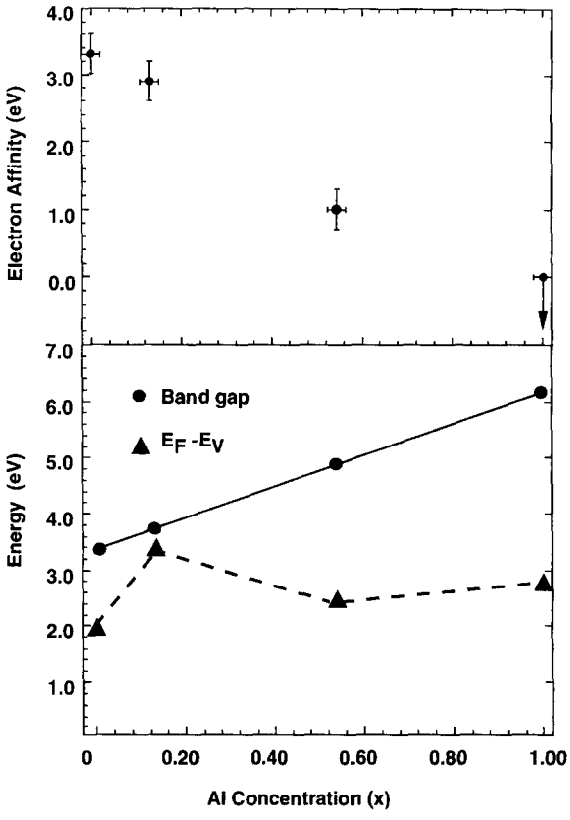

Fig. 7. The dependence of the electron affinity (upper panel), bandgap (filled circles) and surface Fermi level position (triangles) for the AlGaN alloys. The electron affinity and surface Fermi level are obtained from the UPS spectra of Fig.6.

of Al with oxygen may result in increased oxygen incorporation at the surface or in the bulk of these films.

The deduced electron affinities versus alloy concentration are shown in Fig.7. Again we note that the photoemission measurements cannot be used to determine the position of the vacuum level for a NEA surface. Therefore, the electron affinity of the the AlN is indicated at $\chi=0$ with an arrow to larger negative values. The results suggest that the electron affinity depends on the alloy concentration. It should be noted that we have made no effort to control the surface termination for these samples. As shown above for diamond, it was found that the observation of a NEA is critically dependent on the surface termination. Future studies will explore whether the electron affinity of AlGaN materials is also affected by different surface preparations.

5. Electron emission from a negative electron affinity surface

The major device related goal of these studies is the development of a cold cathode electron emitter. Three steps can be considered in understanding the emission process: (1) electron supply to the semiconductor, (2)

transport from the supply electrode to the surface, and (3) the emission into vacuum. This study has focused only on the last of these processes. Other measurements such as field emission involves all three process and secondary electron emission which largely involves steps 2 and 3.

There have been many studies of field emission from point emitters (Spindt tips). The sharp point emitters result in a field enhancement at the tip and a possible reduction in the work function due to the steps on the surface. The current versus voltage from a field emitter follows the Fowler-Nordheim expression.

In contrast, the I–V dependence of an ideal NEA based emitter would exhibit emission at any (negative) voltage. At low fields the current would be limited by the space charge in the vacuum around the emitter (following Child-Langmuir dependence) and at higher voltage the current would be limited by the resistance of the semiconductor and the contact. The energy distribution of the emitted electrons from a NEA cathode should be very narrow (kT), and it should exhibit a noise component related to the resistance of the semiconductor and contact. This is in contrast to either thermal emitters (i.e. hot cathodes) or field emitters that exhibit fluctuations based on the statistics of the highest energy part of the electron distribution.

An electron emitter based on a negative electron affinity material would have several unique advantages over pointed field emitters. These would include low turn on voltage, high current, low erosion, and low noise. In addition the field emitter requires a significant field established through a potential between the tip and a nearby grid layer. In contrast, the NEA device would be controlled by a small field established by the grid to balance the anode to cathode field.

6. Concluding remarks

The results presented here demonstrate that a negative electron affinity surface can be obtained for diamond and other wide bandgap semiconductors. Fig.8. summarizes the hexagonal lattice constant and bandgap dependence for the nitride and carbon related materials. We also show on this figure the materials that have been shown to exhibit a NEA. In addition to the measurements described here, recent results have also demonstrated that BN exhibits a negative electron affinity [22,23]. It is interesting to note that all materials from this group with a bandgap larger than diamond exhibit an negative electron affinity.

For development of cold cathodes, the electron supply may be as critical as the emission properties. Future studies of diamond will focus on methods to supply electrons to the conduction band. Certainly n-type diamond would be an important breakthrough.

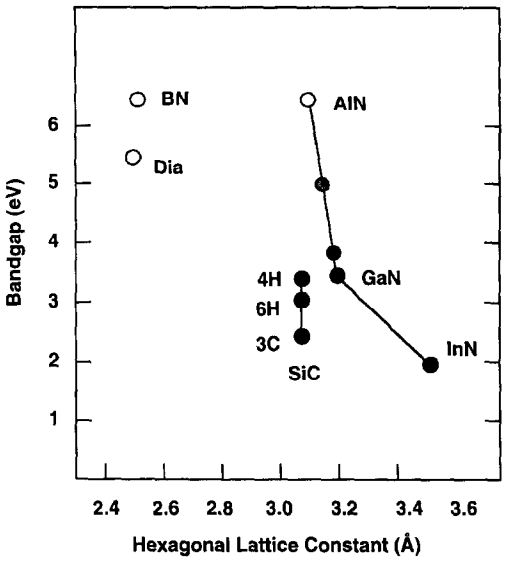

Fig. 8. The bandgap vs. hexagonal lattice constant for a group of wide bandgap semiconductors. For the cubic materials, the lattice constant is the unit cell in the (111) plane. The open circles represent materials that have been shown to exhibit a negative electron affinity.

Studies of nitride surfaces are just beginning, but important issues here are also related to n-type doping. While Si is an effective n-type dopant for GaN, we have not observed n-type surfaces for the Al rich AlGaN films. An important future study will be the measurement of the electron affinity of a series of well characterized AlGaN alloys, and the experimental progress should be paralleled with theoretical studies. These measurements may lead to a better understanding of the relative role of the band gap of the semiconductor and the surface termination.

Acknowledgments

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References

[1] S.P. Bozeman, P.K. Baumann, B. Ward, R.J. Nemanich, and D. Dreifus, *Diamond Relat. Mater., 5* (1996) 802.
[2] A. Zangwill, Physics at Suface, 1988, Cambridge.
[3] F.J., Himpsel, J.A. Knapp, J.A. van Vechten and D.E. Eastman, *Phys. Rev. B20,* (1979) 624.
[4] B.B. Pate, *Surf. Sci., 165* (1986) 83.
[5] J. van der Weide, and R.J. Nemanich, *Appl. Phys. Lett., 62* (1993) 1878–1880.
[6] C. Bandis and B.B. Pate, *Phys. Rev. Lett. 74,* (1995) 777.
[7] P.K. Baumann, T.P. Humphreys and R.J. Nemanich, in C.H. Carter, G. Gildenblat, S. Nakamura, R.J. Nemanich (eds.), Diamond, SiC and Nitride Wide Bandgap Semiconductors, *Mater. Res. Soc. Proc. 339,* Pittsburgh, PA (1994) 69.

[8] J. van der Weide, Z. Zhang, P.K. Baumann, M.G. Wensell, J. Bernholc and R.J. Nemanich, *Phys. Rev. B, 50* (1994) 5803.
[9] P.K. Baumann and R.J. Nemanich, *Diamond Relat. Mater., 4* (1995) 802.
[10] J. van der Weide and R.J. Nemanich, *Appl. Phys. Lett., 62* (1993) 1878.
[11] J. van der Weide and R.J. Nemanich, *Phys. Rev. B, 49* (1994) 13629.
[12] J. van der Weide and R.J. Nemanich, *J. Vac. Sci. Technol. B 10* (1992) 1940.
[13] P.K. Baumann and R.J. Nemanich, *Proc. of the 5th Int. Conf. on the Formation of Semiconductor Interfaces, Appl. Surf. Sci.,* (1995) in press.
[14] S.C. Erwin and W.E. Pickett, *Surf. Coat. Technol., 47* (1991) 487.
[15] S.C. Erwin and W.E. Pickett, *Solid State Commun., 81* (1992) 891.
[16] W.E. Pickett and S.C. Erwin, *Phys. Rev. B, 41* (1990) 9756.
[17] W.E. Pickett and S.C. Erwin, *Superlatt. Microsruct. 7* (1990) 335.
[18] W.E. Pickett, M.R. Pederson and S.C. Erwin, *Mater. Sci. Eng. B, 14* (1992) 87.
[19] W.R.L. Lambrecht, *Physica B, 185* (1993) 512.
[20] M.C. Benjamin, C. Wang, R.F. Davis, R.J. Nemanich, *Appl. Phys. Lett., 64* (1994).
[21] M.C. Benjamin, C. Wang, R.S. Kern, R.F. Davis, R.J. Nemanich, *Mat. Res. Soc. Symp., 339* (1994) 81.
[22] M.J. Powers, M.C. Benjamin, L.M. Porter, R.J. Nemanich, R.F. Davis, J.J. Cuomo, G.L. Doll and Stephen J. Harris, *Appl. Phys. Lett. Diamond Relat. Mater., 5* (1996) 326.
[23] C. Bandis, W-Y. Chang, B.B. Pate, *67* (1995) 3912.