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Interface Reactions of Titanium on Single Crystal and Thin Film Diamond Analyzed by UV Photoemission Spectroscopy

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Abstract

The reactions of titanium on natural crystals and CVD polycrystalline thin films were studied by uv-photoemission spectroscopy. The focus of this study was to characterize the interface reactions and to determine the Schottky barrier of titanium on diamond, deposited and annealed in UHV. Spectroscopic features attributed to the electronic states of Ti-C were identified, and the formation of titanium carbide was observed as a function of annealing temperature. The onset of a titanium-carbon reaction was observed after the 400°C anneal. A well defined TiC spectra was observed after annealing to 600°C. The Schottky barrier height from Ti on natural p-type diamond (111) was obtained by determining the valence band maximum and the Fermi level, and a barrier height of 1.0±0.2 eV was found.

Introduction

Along with the rapidly advancing field of CVD diamond thin films for electronic applications, there is an increased interest in metal contacts on diamond. These contacts can be either ohmic or rectifying, depending on the metal, surface preparation prior to metal deposition and treatment of the contact [1]. Titanium is known to form a Schottky contact on diamond when deposited at low temperatures but is generally used to form an ohmic contact by annealing the contact above 580°C [2,3], or by depositing the titanium while the diamond is kept at 400°C [4]. The transition from rectifying behavior to ohmic behavior after annealing has been shown for carbide forming metals [2]. In this study we have employed angle resolved uv-photoemission spectroscopy, (ARUPS), to observed the onset of titanium carbide formation for UHV deposited titanium films on both single crystal diamond and diamond thin film.

Although there have been many reports of the rectifying behavior of titanium on diamond, to our knowledge no measurements of the Schottky barrier height have been reported. Due to the high ideality factor of the titanium-diamond rectifying contact it is generally difficult to determine the Schottky barrier height using I-V measurements. The position of the valence band maximum on the surface of diamond relative to the Fermi level of a titanium film can be determined from the ARUPS data. The energy difference is the Schottky barrier height for the metal on a p-type semiconductor. This technique was used to determine the Schottky barrier height for UHV

deposited titanium on both diamond thin film and single crystal, type IIB, diamond with a (111) orientation.

Experimental

The ARUPS data was measured with a 50mm hemispherical analyzer with an ultimate energy resolution of 0.02eV and an angular resolution of 2°. The analyzer is mounted on a two stage goniometer which allows angle dependent measurements. As an excitation source a differentially pumped helium discharge lamp was used, which generated HeI (21.2eV) radiation. The base pressure of the ARUPS chamber was $<1 \times 10^{-9}$ Torr with an operating pressure of 5×10^{-9} Torr. The sample was mounted on a heating stage which allows the samples to be annealed up to ~1000°C. The ARUPS chamber is equipped with a Ti-filament deposition source. The pressure during deposition was $\sim 5 \times 10^{-8}$ Torr which dropped rapidly after the filament was turned off. The samples can be transferred from the ARUPS chamber under UHV conditions into a rf-plasma chamber. Both argon and hydrogen plasmas were employed to clean the diamond surfaces.

The single crystal diamond wafers, 3x3x0.5 mm, type IIB, with (111) orientation, were polished in 0.25 μm diamond grid and chemically cleaned prior to loading into the vacuum. The chemical cleaning procedure consisted of a 10 min. etch in fuming sulfuric acid, to remove wax used to hold the diamond in the polishing process, a 45 min. etch in fuming chromic acid, to remove graphitic material and concluded by a 10 min. etch in aqua regia to remove metal contaminants. The chromic acid was produced by saturating sulfuric acid with CrO_3. Once in vacuum the sample was further cleaned in a H and Ar plasma before Ti was deposited. The diamond thin films used in this study were grown in a hot filament system. These samples were loaded into the vacuum without *ex situ* cleaning. The samples were however annealed *in situ* to above 750°C for 10 min. and exposed to an H/Ar plasma for 30 min. prior to Ti deposition. All the samples were mounted with Ta wire on a Molybdenum sample holder. Spectra were obtained for increasing titanium coverages until the diamond features in the spectrum were totally replaced by Ti features. For the annealing study a 30Å layer of Ti was deposited and consequently annealed at increasing temperatures in 100°C increments, for 5 min., after which spectra were obtained.

Results and Discussion

In order to determine the Schottky barrier height from ARUPS data, it is necessary to determine the position of the valence band edge in the spectra. The uv-photoemission spectrum of single crystal diamond C(111) at surface normal emission is shown in Fig. 1. The valence band edge can be clearly distinguished by the onset of emission at about 1 eV below the Fermi level. The valence band edge position was determined by linear extrapolation of the slope to zero and was found to be 8.1 eV above the strong peak near 8.5 eV. The valence band position was expressed relative to this peak since it remained visible for increasing titanium coverages. In the same figure a spectrum is shown of the C(111) surface at an angle of 30° off normal along the [110] direction. In this spectrum, the onset of emission shifted -0.6 eV while the strong peak shifted +0.3 eV, the difference between the onset of emission and the reference peak is found to be 7.2 eV. We suggest that the differences in the onset are caused by a downward dispersion of the valence band edge

away from the Γ point in the bandstructure [5]. The spectrum at surface normal emission reflects the valence band at the Γ point and shows therefore the valence band maximum. A spectrum of a diamond thin film is shown in Fig. 1. For the film, the onset of the emission appears at 7.5 eV above the main peak. We suggest that this is due to the fact that the diamond thin film consists of randomly oriented crystals, which makes the spectrum of diamond thin films in effect equivalent to an angle integrated spectrum of single crystalline diamond. The relative energy of the valence band to the strongest feature of the ARUPS for single crystal diamond at normal emission angle was therefore used to determine the valence band maximum. The determination of the valence band maximum and hence the Schottky barrier height is less accurate however, since the position of the main peak is also angle dependent, as noted above.

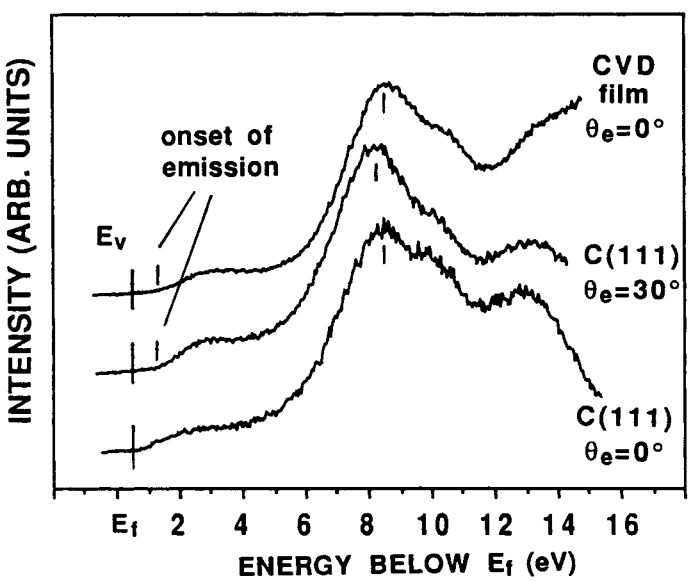

Fig. 1 ARUPS spectra of C(111) at normal emission and at 30° off normal, along the 110 direction and of diamond thin film. The solid line shows the position of the valence band maximum, derived from the onset of the C(111) spectrum at surface normal. The vertical lines show the onset of the of the other spectra.

In order to determine the Schottky barrier height, titanium was deposited at room temperature on the single crystal diamond (Fig. 2) and the diamond thin film (Fig. 3). After the first deposition of titanium on the C(111) surface no titanium features could be discerned although the spectrum shifted by 0.45 eV toward lower energies. After further deposition a sharp Fermi edge developed, due to emission from the d-band of titanium. The diamond

valence band energy was determined using the method described above, and a barrier height of 1.0±0.2 eV was deduced. Following the first deposition of <1Å of titanium on the diamond thin film, no titanium could be detected in the ARUPS spectrum, and the spectrum was found to shift 0.35 eV toward lower energies. After further titanium deposition the Fermi level developed while the diamond features were attenuated but still visible. Again, from these spectra, the diamond valence band maximum was determined, and a Schottky barrier height of 0.9 (+0.5/-0.2) eV was found for titanium on the diamond thin film. The asymmetry in the error is related to the fact that the main peak position is angle dependent.

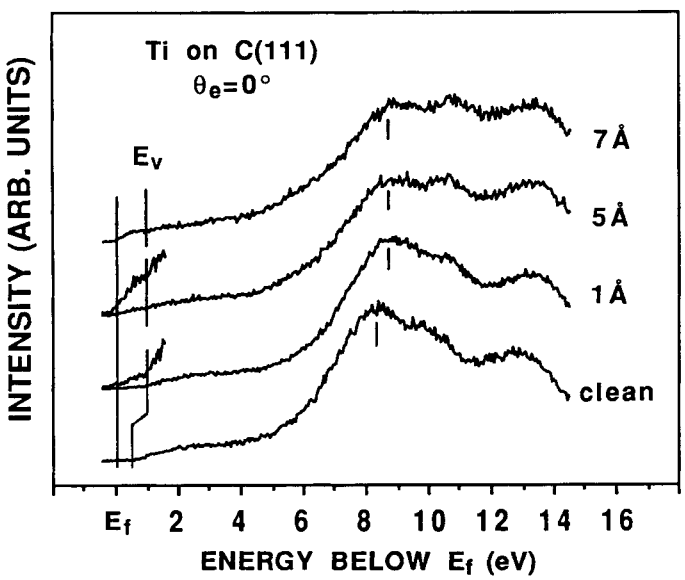

Fig. 2 Normal emission spectra of C(111) as a function of titanium coverage.

ARUPS spectra of the annealing of a 30Å layer of titanium on a diamond thin film are shown in Fig. 4. The emission at the Fermi edge is again due to the titanium d-band. It has been suggested that the broad peak near -5.5 eV is due to a contamination of the deposited titanium layer, possibly oxygen or hydrogen [6]. No diamond features could be discerned. Subsequent spectra were obtained after annealing the film at increasing temperatures, at 100°C increments. After annealing the film to 400°C a peak starts to appear around -3.5eV and gets more pronounced after annealing to higher temperatures for 5 minutes at a time. This peak is associated with Ti-C bonding [6] and shows the development of Ti-carbide formation which reaches its completion after a 600°C anneal. This correlates well with the transition from rectifying behavior to ohmic behavior as described by Gildenblat [3].

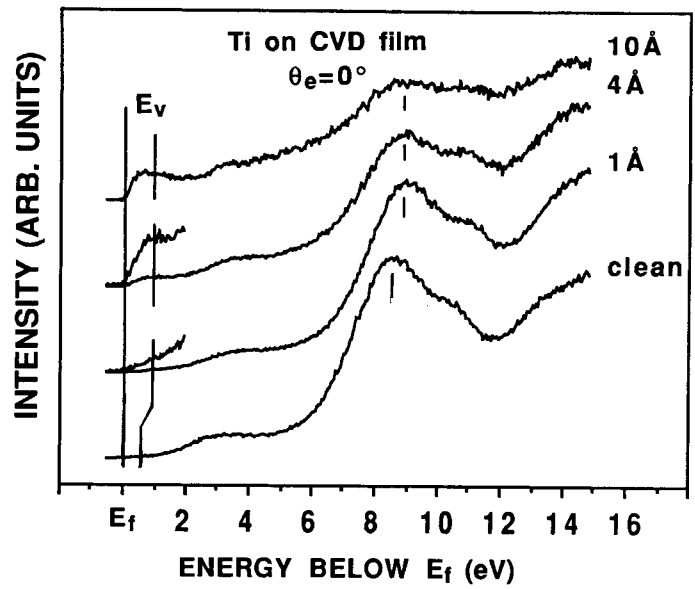

Fig. 3 Normal emission spectra of diamond thin film as a function of titanium coverage.

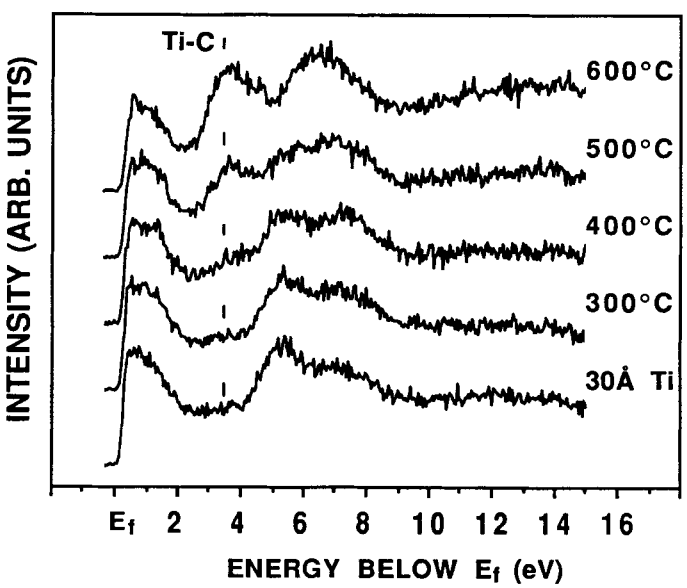

Fig. 4 Normal emission spectra of diamond thin film with 30Å Ti as a function of annealing temperature. The peak appearing at 3.5 eV below the Fermi level is indicative of Ti-C formation.

Summary

Using ARUPS the Schottky barrier height was determined for titanium on both single crystal diamond and diamond thin film. The Schottky barrier height of titanium on single crystal diamond was found to be 1.0±0.2 eV which compared well with the value of 0.9 (+0.5/-0.2) eV found for titanium on diamond thin film. Also the transition from titanium to titanium-carbide was observed to occur for a 30Å layer of Ti on diamond thin film after a 600°C anneal. The onset of the interface reactions were observed at 400°C.

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