Total Photoyield Spectroscopy Experiments on Hydrogen- and Oxygen-Terminated Diamond Films

D. Takeuchi

Diamond Research Center, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, 305-8568, Japan

(Received 29 March 2005; accepted 31 May 2005)

Key words: diamond, surface termination, negative electron affinity, surface conductivity, n-type, total photoyield spectroscopy

We discuss total photoyield spectroscopy (TPYS) results by characterizing not only p-type and intrinsic single-crystal diamond, but also show data from n-type single-crystal diamond, which has hydrogen and oxygen terminated surfaces. After introducing experimental conditions and details of TPYS with a Au film, we discuss total photoyield results from hydrogen-terminated intrinsic diamond based on termination conditions, thickness, and surface conductivity. Above band-gap (5.5 eV) excitation energies, total photoyield on hydrogen-terminated p-type and intrinsic diamond are represented the bulk-related properties, which are expected properties of negative electron affinity. Below 5.5 eV, a unique threshold at 4.4 eV is observed for all samples. This feature results from optically induced transitions of electrons from the valence-band in or close to the surface into the vacuum level. On the basis of these interpretations, a hydrogen-terminated n-type diamond surface also has a negative electron affinity, and TPYS experiments can detect the energy separating the vacuum level and the valence-band maximum. We also find that n-type doping of hydrogen-terminated diamond results in an upward surface band bending in the vicinity of the surface, which acts like a positive electron affinity by preventing electrons in the conduction band from being emitted without a barrier.

*Corresponding author: e-mail: d.takeuchi@aist.go.jp
1. Introduction

On the basis of its unique electronic properties, diamond is a promising wide-band-gap semiconductor with an optical gap of 5.5 eV.\(^1,2\) Moreover, hydrogen-terminated (H-terminated) diamond is one of the most promising materials for cold-cathode emitters due to its high electron emissivity with a negative electron affinity (NEA).\(^3\)

Chemical vapor deposition (CVD) of homoepitaxial diamond films is a promising technique to grow high-quality diamond with respect to optical and electronic properties.\(^4,5\) One of the most remarkable advances in the last ten years has been the development of n-type doping using phosphorus.\(^6,7\) The n-type diamond is highlighted as the material of choice for field emitters.

The NEA of diamond has been discussed qualitatively using bright images of secondary electron microscopy (SEM), a large and sharp thermalized secondary electron peak in X-ray-induced photoelectron spectroscopy (XPS) or ultraviolet-light-induced photoelectron spectroscopy (UPS).\(^3\) Due to the larger electronegativity of carbon than that of hydrogen, C-H forms a dipole which is considered to be the origin of the NEA of the hydrogen-terminated diamond. In the case of an oxidized diamond surface, the dipole is reversed which is expected for a positive electron affinity (PEA).\(^8,9\)

Electron affinity is an important parameter in the performance of electron emission devices; however, the reported values have not yet been concluded, and the details of electron affinities on diamond surfaces are still under discussion.\(^9\) Especially for the n-type diamond, although during the last ten years n-type diamond has been continuously improved, the characterization of H-terminated n-type diamond is still incomplete.

Only a few experimental techniques are suitable for the routine quantitative evaluation of NEA.\(^8\) Such knowledge is highly desirable in order to exploit fully the potential of diamond for electron emission devices.

In total photoyield spectroscopy (TPYS), the quantum efficiency of photoelectron emission is measured as a function of photon energy.\(^10\) TPYS is able to reveal a “positive” electron affinity (PEA) in materials by detecting the onset of photoyield, taking into account the band gap of semiconductors under investigations.\(^11,12\) In the case of p-type H-terminated diamond samples which are expected to have NEA surfaces, a clear onset of total photoyield (TPY) at a band-gap excitation energy of \(h\nu = 5.5\) eV was reported.\(^13,14\) From this point of view H-terminated diamond has been discussed as an NEA sample on the basis of TPYS; the vacuum level position is equal to or lower than the conduction band (CB) minimum. Several TPYS reports also pointed out that H-terminated diamond usually shows a unique photoyield threshold at 4.2–4.5 eV.\(^14,15\) The relationship between NEA and this sub-band photoyield is however still under discussion so far.\(^16\)

In the case of H-terminated diamond surfaces, the so-called p-type surface conductivity (SC) must also be taken into account to discuss photoyield properties.\(^17,18\) The sheet conductance of SC reaches values as high as \(10^{-5}\) S (\(\Omega^{-1}\)) per square, independent of whether the diamond is single crystalline or polycrystalline, prepared by chemical vapor deposition. This SC is unique among all semiconductors and insulators, and it has already been utilized for a variety of devices such as Schottky diodes,\(^5\) field-effect transistors,\(^19,20\) and pH sensors.\(^21\) The phenomenon is based on a surface-near hole layer with a concentration on
the order of $10^{12} - 10^{13}$ cm$^{-2}$ that shows little temperature dependence and thus one of three models requires acceptors that are very shallow above or even degenerate with the VB.$^{(15,22,23)}$

In this paper, we discuss TPYS results deduced by characterizing not only p-type and intrinsic diamond, but also n-type single-crystal diamond, with hydrogen- or oxygen-terminated surfaces.$^{(2,9)}$ In the next two sections we introduce the experimental conditions and details for TPYS. Then, we discuss the effect of thickness on TPY in § 4.1, followed by the effect of SC on TPY in § 4.2. Taking into account the Fermi-energy dependence of TPYS, we discuss the photoyield threshold at 4.4 eV, and carry out a quantitative evaluation of electron affinities of H-terminated diamond of the p-type, intrinsic and n-type in § 4.3. Finally we summarize this paper.

2. Total Photoyield Spectroscopy

In TPYS the quantum efficiency of photoelectron emission is measured as a function of photon energy. A schematic diagram of our TPYS system is shown in Fig. 1. A Xe arc lamp and a D$_2$ lamp are used as light sources, which can be selected using a shutter in the optical system. Monochromatic light is focused on the samples in a UHV chamber, and photoelectrons are collected by an electron multiplier tube (Channeltron: BURLE Electro-Optics, Inc.) attached in the same chamber. The intensity of the light is measured using a beam splitter (MgF$_2$) and a photomultiplier tube (PMT). All the optical components are set in shade boxes, which can be purged with dry N$_2$.

Fig. 1. A schematic diagram of our TPYS system. A Xe arc lamp and a D$_2$ lamp are used as light sources, which can be selected by a shutter in the optical system. Monochromatic light is focused on samples in a UHV chamber and photoelectrons are collected by an electron multiplier tube (Channeltron: BURLE Electro-Optics, Inc.). At the same time, a MgF$_2$ beam splitter is used to monitor the light intensity by a photomultiplier tube (PMT). All the optical components are set in shade boxes, which can be purged with dry N$_2$. 
shade boxes, which can be purged with dry N$_2$ to allow the illumination with photons up to 7.5 eV.

It is quite difficult to obtain reliable absolute quantum yields; however, the measured yield from different samples can be compared when the measurement conditions, such as bias parameters of the Channeltron and PMT are kept constant. A typical example to evaluate the reproducibility of data measured using a TPYS on a Au film in the UHV chamber is shown in Fig. 2. The seven spectra obtained during one month are plotted, and a theoretical curve based on the Fowler equation for Au at 300 K is also shown. As seen in this figure, all the measured data points are almost comparable. The theoretical curve fits the experimental data very well, which is used to calculate the work function of Au, to be 4.365 eV. This number is significantly lower than the 5.3 eV given in handbooks, which has been measured on “clean” Au surfaces.$^{(24)}$ Au surfaces transferred through the air show lower work functions when Au is placed in UHV with neither fresh evaporation nor ion sputtering.

Fig. 2. A typical example to evaluate the reproducibility of data measured using TPYS on a Au film in a UHV chamber. The seven spectra are obtained during one month. Also shown is a theoretical curve based on the Fowler equation for Au at 300 K.
To characterize the thickness dependence of total photoyield (TPY), we used a synthetic type-IIa (intrinsic) diamond with (001) crystal orientation, and an undoped CVD film (001). The thickness of IIa is 300 μm and that of the CVD film 0.15 μm. The CVD film was grown on synthetic type Ib (001) diamond (Sumitomo Co., Ltd.), which had misorientation angles of less than 1°, under ultralow growth rate conditions to achieve a high-quality semiconductor.(4) The samples were cleaned by boiling in a mixture of H₂SO₄ and HNO₃ at 230°C to remove nondiamond carbon and to oxidize the surfaces. After that, samples were H-terminated in a microwave hydrogen plasma at 800°C. For TPYS measurements, the samples were mounted on a molybdenum (Mo) sample holder with a tantalum (Ta) cover and were introduced into a UHV system at a base pressure of 8×10⁻⁹ Pa. Before TPYS experiments, these samples were annealed in UHV to get rid of surface conductivity.(15) TPYS was carried out at RT.

To identify effects which arise from doping (p-, intrinsic, and n-type), we used a synthetic type IIa (intrinsic) diamond with (001) crystal orientation, a synthetic type Ib (N-incorporated at a substitutional site as a very deep donor) diamond with (111) orientation, a B-doped p-type CVD film (111) (CVD-B), and a P-doped n-type CVD film (111) (CVD-P). All of the samples were single crystalline. The thickness of IIa is 300 μm, of Ib 500 μm, of CVD-B 0.75 μm, and of CVD-P 2 μm. The CVD films were grown on synthetic type Ib (111) diamonds (Sumitomo Co., Ltd.), which had misorientation angles of 2°–3°. The electronic properties (p-type for CVD-B and n-type for CVD-P) were confirmed by Hall-effect measurements at RT. The type Ib diamond was n-type at temperatures higher than 350°C. The samples were cleaned by boiling in a mixture of H₂SO₄ and HNO₃ at 230°C to remove nondiamond carbon and to oxidize the surfaces. After that, samples were H-terminated in a microwave hydrogen plasma at 800°C. For TPYS measurements the samples were mounted on a molybdenum (Mo) sample holder with a tantalum (Ta) cover and introduced into a UHV system at a base pressure of 8×10⁻⁹ Pa. TPYS was carried out at RT without application of a prethermal annealing to remove adsorbates.

### 4. Results and Discussion

#### 4.1 Dependence of TPY on thickness

The physical models for photoelectron emission from NEA surfaces have been discussed by Spicer. In the absence of any barrier between the conduction band minimum (CBM) and the vacuum level, i.e., for NEA surfaces, thermalized electrons after photoexcitation can contribute to photoyield, and the escape depth of electrons is not limited by the thermalization length, but instead by the much longer diffusion length of electrons. The total photoyield is given by

\[
Y(h\nu) = \sum \eta_i L_i \alpha_i(h\nu) \\
1 + L_i \alpha(h\nu),
\]  

(1)
where $\alpha(h\nu)$ is the absorption constant, $\eta$ the escape probability, and $L$ the diffusion length. The $i$ in eq. (1) represents each absorption component, and

$$\alpha(h\nu) = \sum_i \alpha_i.$$  \hspace{1cm} (2)

For band-edge photoexcitation, it was reported that excitons also contribute to the yield.\textsuperscript{(13,14)} Diamond is an indirect semiconductor. The generation of excitons requires therefore a photon and a phonon interaction, dominated by coupling with transverse optical phonons (TO-phonon). Details have been reported by Cui et al.\textsuperscript{(16)}

Figure 3 shows TPYS results both for a IIa (001) bulk sample and for a CVD homoepitaxial (001) thin film. The data were normalized at 5.2 eV. The open circles represent data of IIa, and filled circles of the undoped CVD film.

Below 5.5 eV, which corresponds to the band-gap energy of diamond, both samples show comparable spectra. For energies larger than 5.5 eV a distinct difference can be detected. The amplitudes differ by an order of magnitude. The Ib substrate of the CVD film could not show this onset because an energy barrier at the junction between the n-type nature of the Ib substrate and the undoped intrinsic CVD film prevents electron diffusion from the Ib substrate into the CVD film, and also because the Ib substrate is such a defective material that photoexcited free electrons do not have enough lifetime to diffuse.

When the effect of thickness is taken into account in Spicer’s model, eq. (1) becomes

![Fig. 3. TPY spectra of plasma H-terminated IIa (001) and of undoped CVD (001) thin film. The data were normalized at $h\nu=5.2$ eV. The open circles represent data of IIa, and filled circles of the undoped CVD film. Both samples were annealed in UHV to get rid of high surface conductivity.](image-url)
\[ Y_i(h\nu) = \frac{\eta_i L_i \alpha_i(h\nu)}{1 + L_i \alpha_i(h\nu)} \left\{ 1 - \exp(-\alpha_i(h\nu)) + \frac{1}{L_i} d \right\} \]  

(3)

where \( d \) is the thickness of the CVD film on the Ib substrate. If we assume the exciton or electron diffusion length in CVD \( L_i^{\text{CVD}} \) \((i = \text{“exciton” or “electron”})\) is much larger than \( d \) (~150 nm), then eq. (3) gives us the exciton or electron diffusion length. According to these analyses, the \( L_i \) in diamond should be at least in the range of micrometers.

4.2 Surface conductivity

One of the most important properties of H-terminated diamond is the surface conductivity (SC). As described in § 1, the SC behaves like a \( p^+ \) semiconductor with a very strong sensitivity on adsorbate.\(^{26,27}\) In order to investigate the relationship between SC conditions and TPY, a IIa (001) sample was measured using TPYS.

Figure 4 shows TPY spectra of IIa (001) diamond. Both spectra are normalized at \( h\nu = 5.2 \) eV. The first spectrum was taken after being freshly hydrogenated (open circles), the other after annealing at 350°C (open triangles). This temperature is sufficient to eliminate SC.\(^{28}\)

Below 5.5 eV, both sub-band TPY spectra are identical as shown in Fig. 3. Above the 5.5 eV excitation regions, both samples show clear rises at 5.5 eV, which coincides with the band-gap energy of diamond and proves the NEA of hydrogenated surfaces.\(^{3,14}\) However,
the degree of increase after annealing is almost one order of magnitude larger than that of the as-hydrogen-terminated sample. In addition, the spectrum of the as-hydrogenated sample shows oscillatory yield whereas the experiments do not show strong oscillations after thermal annealing in UHV. These results are in good agreement with previously reported results.\(^{(15)}\)

The experimental results presented here clearly establish that an electron diffusion barrier towards the surface exists in the case of high surface conductivity that vanishes after annealing as shown in Fig. 5. Figure 5 shows schematic energy band diagrams of a diamond surface at high and low surface conductivities with photoexcitation processes. The horizontal axis corresponds to the depth on the scale of micrometers, the vertical axis to energy, \(E_c\) to the energy level of the conduction band minimum, \(E_v\) to the valence band maximum, \(VL\) to the vacuum level, and \(\chi\) to the electron affinity.

On the left side of Fig. 5 the case with SC is shown. Hla is an intrinsic material. We expect an upward band bending towards the surface.\(^{(15,29,30)}\) This upward band bending prevents electrons from diffusing to the surface so as to contribute to the yield.

The right side of Fig. 5 represents the case without SC.\(^{(15,29,30)}\) Here the energy diagram is for flat band conditions; however, a downward band bending is also allowed. The key issue here is that there is no barrier for electrons, which are photoexcited and can therefore contribute to the yield.

According to the discussion in § 4.1, the diffusion length of electrons is on the order of micrometers.

We now turn to the emission above 5.5 eV in the case of the as-hydrogenated surface. The well-defined step in the TPY spectra at about 5.5 eV is a clear indication that emission with a threshold close to the band-gap energy is superimposed on the surface-related sub-band emission spectrum, which is discussed in the next section. This contribution is obviously not suppressed by the diffusion barrier connected with upward band bending in

![Fig. 5. Schematic energy band diagram of a diamond surface with and without surface conductivity.\(^{(15,29,30)}\) The horizontal axis corresponds to the depth on the scale of micrometers, the vertical axis to energy, \(E_c\) to the energy level of the conduction band minimum, \(E_v\) to the valence band maximum, \(VL\) to the vacuum level, and \(\chi\) to the electron affinity.](image)
samples with a high SC as depicted schematically in Fig. 5. As was first pointed out by Bandis and coworkers, (13,14) excitons as well as free electrons contribute to the TPY of diamond, starting with slightly different thresholds around the band-gap energy of 5.5 eV as mentioned in § 1. An oscillatory yield spectrum is characteristic for the exciton contribution. The oscillation is a result of the thermalization process after photoexcitation via multiple emissions of optical phonons. Depending on the photon energy, the thermalization process leaves the exciton with a final kinetic energy between zero and the energy of the optical phonon (160 meV) that determines the break-up probability of the excitons. (1,13) Therefore, the spectral oscillations in Fig. 4 in the as-hydrogenated case identifies the above-band-gap contribution as exciton mediated. Clearly, excitons as neutral entities are not affected by band bending. In this sense, their contribution to the yield of the samples with high SC and upward band bending strengthens our interpretation of the changes in TPY with SC. For samples with low SC (after annealing), the oscillatory exciton contribution is masked by the much more intense contribution of free electrons. (15)

4.3 Sub-band yield on H-terminated surfaces

As shown in Figs. 3 and 4, the sub-band yield below 5.5 eV is independent of either the thickness of samples or the SC conditions, namely band bending conditions. To study this sub-band yield on H-terminated diamond surfaces, we used four different doped samples. (31) Figure 6 shows the TPYS results of as H-terminated IIa, Ib, CVD-B and CVD-P. The inset is an enlarged figure of the band-gap excitation region of Fig. 6. These data were normalized at 5.5 eV.

As can be seen in Fig. 6, all H-terminated samples show the same threshold energy at 4.4 eV, and the spectra in the energy regime from 4.4 to 5.5 eV are identical, regardless of their nature as p-type, n-type or intrinsic, or of their differences in bulk properties such as absorption coefficient, diffusion length of electrons, thicknesses, or defects. In the case of oxidized surfaces, however, these sub-band spectra cannot be detected. It is reproducibly found that the TPY onset at 4.4 eV is correlated with the H-termination of the diamond surface. (31) This strongly suggests that the sub-band yield starting at 4.4 eV is related to surface phenomena. The most influential parameter for the sub-band yield from 4.4 eV is obviously the surface termination.

As can be seen in the inset of Fig. 6, IIa and CVD-B samples show a pronounced rise at 5.5 eV, corresponding to valence-band (VB) to CB excitation in diamond. This rise of TPY intensity above 5.5 eV of IIa (300 μm) is clearly larger than that of CVD-B (0.75 μm). (15) As the absorption width at 5.5 eV is approximately 10 to 20 μm, the difference in TPY is attributed to the difference in thickness, and thus is a bulk-related effect, as discussed in § 4.1. In the cases of n-type diamond, however, this rise could not be detected at all. Note that the CVD-P showed clear conduction band transport properties at RT. This is surprising, as n-type diamond has been defined as “the electron-emitting semiconductor”. In the case of oxidized surfaces with PEA, neither the onset of TPY at 5.5 eV nor the sub-band yield was observed from any of the samples. In our system, the onset has never been observed and/or has been below the detection limit up to a photoexcitation energy of 6.0 eV.

Figure 7 shows schematically the four photoexcitation paths of electrons into the vacuum level for the case of an NEA surface. (31)
Fig. 6. TPY spectra of plasma H-terminated IIa, Ib, CVD-B, and CVD-P. The inset is an enlarged figure of the band-gap excitation region. The data were normalized at $h\nu=5.5$ eV. The solid line represents data from IIa; the dashed line, CVD-B; the dotted line, CVD-P; and the solid line with open circles, Ib. All samples show a threshold around $h\nu=4.4$ eV when the surfaces are H-terminated.

Fig. 7. Schematic description of four photo excitation mechanisms in a diamond with an H-terminated surface. CBM is the conduction-band minimum, VBM the valence-band maximum, and VL the vacuum level. Path IV is discussed as a new and most plausible mechanism for the sub-band yield in this paper. Details are discussed in text.
I. Photoexcitation from occupied defect states in the band gap into CB and diffusion to the NEA surface. This transition depends on the Fermi-level position.

II. Photoexcitation from occupied surface states in the band gap into the vacuum level. This is also a Fermi-level-dependent transition.

III. Photoexcitation from VB into CB and diffusion to the NEA surface. The efficiency of electrons reaching the vacuum level depends on the band bending at the surface (see Fig. 8).

IV. Direct photoexcitation from VB states in or close to the surface into the vacuum level.

In this report, we present data which show that all H-terminated diamond films have a photoyield threshold energy at 4.4 eV, independent of specific doping properties, namely, conduction type and surface band bending. A similar sub-band photoyield in TPY was reported by Cui et al.(16) They applied XPS, a Kelvin probe and TPYS to natural H-terminated IIb diamond. They proposed an inhomogeneous model where areas of NEA H-terminated diamond surface and PEA graphitic patches interact electronically in addition to that depicted as path II in Fig. 7. However for a change from p- to n-type material, this model is not applicable. For n-type diamond, the gap between the Fermi-level and the vacuum level on the surface decreases significantly. Thus, a shift in the onset in the sub-band TPY should be detected, which is not the case.

The universal feature of the photoyield threshold at 4.4 eV originates from surface properties related to the H-termination of the diamond surface, which does not depend on the Fermi level. Thus, the direct photoexcitation from VB electrons in or close to the surface into the vacuum level, as depicted in Fig. 7 as path IV, is considered the most likely transition mechanism. This transition is detected as an intrinsic property of an NEA surface regardless of the conduction type and the surface band bending.

The new photoexcitation model depicted in Fig. 7 as path IV is based on a mechanism which is discussed in the following: The wave functions of photoexcited electrons from the VB in or close to the surface have a finite probability of coupling to vacuum states due to

---

Fig. 8. Schematic images of the band diagram near the surface region and photoelectron transport in conduction band in p- and n-type samples. Details in the case of n-type are discussed in the text.
the photoabsorption of energies equal or larger than the gap between the VB maximum and the vacuum level. The overlapping of these two wave functions determining the sub-band photoyield should be taken into account by the surface structure related to C-H dipoles, which will be clarified in a future report. The details of such transitions have not been discussed mathematically up to now in the literature to our knowledge and therefore need further investigation. According to these discussions, oxidized surfaces with C-O dipoles result in PEA, which are not showing the sub-band photoyield.

Based on our model, the threshold at 4.4 eV is the energy gap between the vacuum level and the VB maximum. Taking into account the 4.4 eV, the NEA is –1.1 eV since the band-gap of diamond is 5.5 eV at RT. An accurate number should be calculated with an equation which describes the detailed mechanism of this new photoexcitation path. Here, this demonstrates that TPYS experiments can reveal the NEA, if the sub-band-gap excitation is not dominated by additional defects. This method can be applied universally for any material, from NEA to PEA.

Our data show a rise of photoelectron emission for excitations around 5.5 eV on p-type and intrinsic H-terminated diamond. For such excitations, VB electrons are excited into the CB, and immediately thermalized to the CB minimum.\textsuperscript{(13,14)} A fraction of the electrons can diffuse to the surface and get emitted from the surface in the case without SC. Exciton-derived photoelectron emission also contributes to this rise, which appears clearly in the case with SC as described in § 4.2. Excitons are generated by photoexcitation, and diffuse to the surface. Finally, they break-up in or close to the surface, a fraction of electrons is generated in the CB minimum, and subsequently they get emitted from the surface.\textsuperscript{(13,14)} The rise, therefore, has been attributed to electrons from the CB minimum. Thus, the electron affinity is assumed to be less than (NEA) or equal to zero because no barrier exists for electron emission from a CB minimum to the vacuum level.\textsuperscript{(13–15)} This interpretation is consistent with our model of sub-band yield and with our quantitative evaluation of an electron affinity of –1.1 eV for H-terminated diamond. In the case of oxidized surfaces with PEA, the onset of TPY at 5.5 eV cannot be observed due to a PEA.

As mentioned previously, phosphorus-doped n-type diamond does not show a rise at 5.5 eV. According to the previous discussion, H-termination of n-type diamond also results in NEA, which originates from C-H dipoles. As no rise at 5.5 eV is detected, we assume that an internal energy barrier prevents electrons from reaching the vacuum. An upward surface band bending is expected, which prevents photoemission from the bulk as schematically shown in Fig. 8. We assume that NEA on n-type diamond allows a fraction of electrons to propagate into the lower vacuum level, until an electric field which arises from ionized phosphorus prevents further out-diffusion. This is comparable to the establishment of a depletion region field in pn junctions. Up to now, however, it is not clear where the out-diffused electrons are. There may be surface defects which can be occupied, adsorbate layers on the surface, etc. Further investigations are needed to elucidate this property.

5. Conclusions

In summary, total photoyield spectroscopy (TPYS) was applied on hydrogen- and oxygen-terminated p-, intrinsic and n-type diamond samples. The summarized photoexcitation processes in TPYS on surfaces of metals, semiconductors with positive electron affinity and
semiconductors with negative electron affinity are shown schematically in Fig. 9.

As demonstrated with Au, TPYS can be applied to detect the electron emission properties of very different samples. Oxygen-terminated surfaces never show any yield in the energy regime of 2 to 6 eV.

On the other hand, hydrogen-terminated surfaces show unique features in total photoyield. Above 5.5 eV total photoyield on hydrogen-terminated intrinsic surfaces are dominated by bulk-related properties such as thickness and surface band bending. The thicker the high-quality region, the larger the amplitude of total photoyield above 5.5 eV. The diffusion length of electrons in diamond can be evaluated, and must be in the range of micrometers.

In the case with surface conductivity, the TPYS spectrum is dominated by photoelectron emission derived with exciton diffusion, as they can propagate without a barrier to the surface. In the case without surface conductivity, the surface electric field is decreased and electrons can also reach the surface, which results in the much higher amplitude of total photoyield above 5.5 eV.

Below 5.5 eV, a unique threshold at 4.4 eV is observed from all high-quality samples. This feature results from optically induced transitions of electrons from the valence band in or close to the surface into the vacuum level. On the basis of these interpretations, TPYS experiments can detect the energy between the vacuum level and the valence-band maximum and can be applied to characterize such surface properties with respect to crystal orientation and termination. We also find that n-type doping of hydrogen-terminated diamond causes an upward surface band bending in the vicinity of the surface, which acts like a positive electron affinity by preventing electrons in the conduction band from being emitted without a barrier.

Acknowledgements

The author is extremely grateful to Prof. Dr. H. Okushi, Prof. Dr. S. Yamasaki, and Dr. C. E. Nebel (Diamond Research Center in AIST) for their perceptive comments and helpful suggestions. Special thanks are also due to Dr. S.-G. Ri and Dr. H. Kato (Diamond Research

Fig. 9. Summary for photoexcitation processes in total photoyield measurements on surfaces of metals, semiconductors with positive electron affinity and semiconductors with negative electron affinity.
Center in AIST) for their many contributions in growing high-quality doped samples. The author would also like to thank Dr. Watanabe (Diamond Research Center in AIST) for H-termination experiments, Dr. Ristein and Prof. Dr. Ley (University of Erlangen) for fruitful discussions about TPYS results, and Dr. Gonda (AIST), Dr. Munakata (RIKEN) and Dr. Yamada (RIKEN) for advice and encouragement in developing the TPYS system.

The author gratefully acknowledges financial support by the NEDO (ADD project).

References