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The role of (sub)-surface oxygen on the surface electronic structure of hydrogen terminated (100) CVD diamond

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In this work, scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS) were applied to investigate the surface morphology and the surface electronic structure of plasma-treated (100)-oriented CVD diamond films. These films were hydrogenated using a conventional MWPE-CVD (microwave plasma enhanced chemical vapour deposition) reactor containing a H_2 or a H_2/O_2 mixture. A comparison is made between (100)-oriented CVD diamond films hydrogenated with and without a small addition of oxygen (1%). X-ray Photoelectron Spectroscopy (XPS) and UV Photoelectron Spectroscopy (UPS) measurements point to the presence of O-atoms at the (sub)-surface of the diamond film. The measured conductivity is significantly different for the two processes of hydrogenation. Annealing experiments point out that the samples, which were terminated using the H_2/O_2 mixture are still conductive enough after annealing at 410 °C to enable STM experiments. Here, we discuss the mechanism for STM imaging of H_2/O_2 treated diamond films, associated with surface states induced by the oxygen incorporation.

Keywords: Diamond properties and applications, surface conductivity, scanning tunnelling spectroscopy, oxygen plasma treatment

1. Introduction

Diamond surfaces terminated by hydrogen and subsequent interactions of the hydrogenated diamond surfaces with ambient environment resulting in the p-type surface conductivity have been intensively studied in the past [1–6]. Maier et al. [7] gave the first experimental evidence that chemisorbed hydrogen is a necessary but not a sufficient prerequisite for such surface conductivity and that the electron acceptors are provided by atmospheric adsorbates, leading to the so called “transfer surface doping” model. Oxygen can play an important role in this process but its influence is not fully understood [8]. The aim of this paper is to elucidate further the mechanism responsible for the surface conductivity and the role of oxygen herein. This effect is very promising because it can be used in future electronic and bioelectronic applications as has been demonstrated on laboratory scale [9–11].

Here, we report on hydrogenation of the diamond surface using a H_2/O_2 mixture during the microwave plasma enhanced surface treatment. The XPS measurement confirms that oxygen is present at the diamond surface. Evidence is given for the beneficial influence of oxygen on the stability of the surface conductivity upon annealing. Especially, even when diamond is annealed at UHV conditions and the atmospheric adsorbate layer disappears, the remaining surface conductivity and surface states induced by the presence of oxygen are enough to enable STM/STS measurements and imaging on the atomic resolution scale. This is not the case for films hydrogenated in a pure H plasma, where after annealing at about 400 °C in UHV, STM/ STS measurements are not possible anymore.

2. Experimental

Single-crystal diamond layers are grown by using the microwave plasma enhanced chemical vapour deposition technique (MWPE-CVD) on (100) Ib orientated HPHT diamond substrates from Sumitomo Electric Ltd. Substrates are cleaned and oxidised before the growth using a mixture of sulphuric acid and potassium nitrite at 300 °C for 30 min. The sample is placed in the vacuum chamber that is pumped down to a vacuum of about 6×10^{-9} Torr. First, a hydrogen plasma is created at 800 °C, at a pressure of 68 Torr, using a power of 500 Wand a hydrogen flow of 500 sccm. After 5 min 1.5 sccm methane is added into the plasma to grow diamond epitaxiaal layers. This growth is carried out for 300 min after which the flow of methane is stopped and only the hydrogen plasma is used for another 5 min. The growth rate is about 1 μm an hour and the resulting film has a roughness of a few nanometers on a micrometer scale, as measured by AFM. After the growth, the single-crystal layer is oxidised chemically by using the same mixture as described above in order to remove all surface contaminants on the diamond surface. After that, the sample is put back into the deposition chamber and the hydrogenation treatment is carried out in a pure hydrogen plasma or eventually with an oxygen addition. For this hydrogenation treatment, we create a plasma at a substrate temperature of 700 °C and a pressure of 75 Torr. A microwave power of 3000 W and a hydrogen flow of 1000 sccm is used and the plasma is kept on for about 30 s after the pressure stabilisation (which takes about 2 min). After removing the sample from the vessel and a subsequent contact of the sample with the ambient the surface resistance drops to about 20–100 $k\Omega/cm^2$ as measured by a two-point contact method and using carbon contacts. Further on we denote layer #1 as a sample hydrogenated in 1% O_2 in H_2 and layer #2 being hydrogenated in pure hydrogen without the oxygen addition. Interestingly, we observe systematically a 10 to 20% resistance lower sheet for samples hydrogenated with H_2/O_2 mixtures. This procedure has been done on different samples for several times leading to identical results. AFM and STM measurements are done using an Omicron UHV STM/ AFM apparatus at room temperature. The annealing of the samples is carried out in situ by a heating element mounted under the sample holder.

3. Experimental results

3.1. Introduction

XPS measurements are used to study the presence of oxygen at the diamond surface after hydrogenation, yielding also information on several bonding configurations of oxygen atoms. The results are shown in Fig. 1. It can be seen that for sample #1 there is a larger oxygen atom coverage than for sample #2 as also can be seen in Table 1. The oxygen presence in sample #2 is ascribed to exposure to air and can be part of the adsorbent layer. As a reference, the XPS results for a chemically oxidized sample also shown in Table 1.

To examine the influence of oxygen on the surface conductivity, annealing experiments are carried out. Sample #1 is placed into the STM in UHV conditions and images are taken before and after two subsequent annealing steps. As can be seen from Fig. 2a, it is very difficult to resolve the surface structure with atomic resolution (scales less then 50 nm). This is probably due to the water adsorbate layer on top of the sample after the hydrogenation process and contact with an ambient environment. The same experiment is repeated after annealing sample #1 for 30 min at 200 °C. From previous works [14,15] it is known that a drop in surface conductivity can be expected when heating the samples to a temperature around 200 °C. In accordance with this fact, it is not possible to do STM imaging after annealing sample #2 for 30 min at a temperature as low as 200 °C. So the surface conductivity and/or the concentration of surface states is not sufficient to provide the tunneling from the tip and the subsequent charge transport to the collecting electrode placed at the edge of the sample. It should be noted that for samples hydrogenated only in a pure hydrogen plasma and exposed to ambient conditions [6] and after an UHV annealing at about 410 °C the surface conductivity undergoes an enormous decline. However, such a drop in the conductivity is not detected for sample #1. After annealing sample #1 in UHV for 30 min at 200 °C, a finer surface structure can be resolved, as can be seen in Fig. 2b. Even a second UHV annealing at 410 °C for 30 min makes it possible to resolve most of the surface structure with carbon dimers, as discussed later, on top of the surface as it can be seen in Fig. 2c.

The imaging is thus only possible for samples hydrogenated in a H_2/O_2 mixture, pointing to the presence of a sufficiently conductive surface and at the same time to the presence of surface states to which electrons from the tip can tunnel which is a necessary prerequisite for STM imaging. From this, we can conclude that the oxygen that was used during the hydrogenation process of sample #1 has an important influence on the surface conductivity and/or on the presence of surface states. A schematic diagram, illuminating the principles for STM imaging via O-induced states are shown in Fig. 3 while the surface band bending is discussed in detail below.

3.2. Surface morphology

STM/STS measurements performed on sample #1 are shown in detail in Fig. 4. Even though similar experiments have been done before, there are several novelties in our measurements compared to previous work [12,13]. Compared to results of Dujardin and Bobrov [12,13] we use undoped H terminated CVD diamond films (in all other published cases either B-doped samples or clean surfaces with a Penney reconstructed surface have been used for STM imaging providing sufficient surface conductivity). Till now, as far as we know it was not possible to carry out STM atomic resolution imaging on annealed H-terminated undoped diamond films. The STM results for sample #1, shown in Fig. 2, were taken using a tip bias U_{bias}=1.5 V and current I=0.80 nA. The surface morphology imaging reveals a very flat surface of the diamond epilayers (a few nanometers roughness on a scale of 10 μm). With an atomic resolution, dimers on top of the layer can be observed. These dimers are the carbon atoms at the top layer, lying in one direction 5.044 Å apart from the next dimers. Also the 2×1 reconstruction can be seen, with dimers lying on terraces sized in the order of 2 nm by 2 nm and rotated to each other by 90°. Measurements on sample #1 demonstrate that the size and orientation of the terraces is not influenced by the addition of oxygen during the hydrogenation as similar results were obtained for H-terminated B-doped diamond in Ref. [12].

Fig. 5 shows the I–V characteristics of the two samples. As can be seen, while the one of sample #2 exhibits a quasi-Ohmic character with no surface bandgap, probably due to adsorption of water —e.g. the H/H_3O_+ terminated surface, which leads to tunneling and current flow through the adsorbants (water) layer. Sample #1 has a surface bandgap of around 3.5 eV after UHV annealing to 410 °C. Fig. 5(c) shows the first and second derivative of the I–V characteristics of the sample #1. Fig. 5c shows a resonance tunneling behaviour, similar to the one observed for clean diamond surfaces in Ref. [12,13]. Nevertheless, in our case, the surface resonances are observed for the hydrogenated surface, containing also residual oxygen atoms while in ref [13], hydrogen-free, 2×1 reconstructed surfaces have been studied. These resonances observed for H_2/O_2 mixture treated diamond surfaces are observed for the first time and will be discussed in another publication.

3.3. Discussion

The presence of levels in the surface bandgap, detected by STS, implies that the tunnelling can occur to such states if at the same time there is a sufficient electrical conductivity to collect the carriers tunnelled from the STM tip into the surface states (see Fig. 3). This could be observed for sample #1. On the other hand, for sample #2 there is not sufficient conductivity and/or concentration of surface states to carry out STM experiments. Because STM imaging was possible for B-doped H-terminated diamond surfaces [12,13] (e.g. there is a sufficient density of Hrelated surface states as reported in several publications [12]), we can conclude that it is probably mainly the surface conductivity that limits the STM imaging on undoped samples hydrogenated in a pure H-plasma and subsequently UHVannealed. This implies that for

our H_2/O_2 mixture hydrogenated sample, as soon as the adsorbate related surface conductivity vanishes after the annealing at temperatures of 410 °C, another mechanism takes over, leading to a remaining sufficiently high electrical conductivity. To study this hypothesis UPS measurements have been carried out to study the surface states for sample #1. In Fig. 6 the He I spectrum for sample #1 is shown. From this spectrum, the work function ψ=3.4 eV can be determined. Further on, a typical peak pointing to negative electron affinity can be observed, i.e. electrons thermalised into the conduction band minimum (CBM) are emitted very easily into the vacuum, appearing in the He I spectrum as a sharp, high-intensity peak at low kinetic energies. Its energy position determines the CBM position [16–18]. So, in case of sample #1 we can observe NEA and a work function of about 3.4 eV which points towards upwards surface band bending (about -1.4 eV in our case determined from the position of the NEA peak). This situation was depicted in Fig. 3. Though the exact model of surface conductivity after a hydrogenation in a H_2/O_2 mixture is still under discussion, we believe that the presence of oxygen, as confirmed by XPS, and the upward band bending, confirmed by UPS, point towards a possible strong coupling of O-surface states, reported previously in the literature [8], into the valence band maximum (VBM) could lead to the electron tunneling from such states to the VBM, and the tunneled charge can be efficiently led out of the sample, leading to sufficient conductivities and consequently possible STM imaging.

4. Conclusion

XPS measurements on CVD diamond films, plasma-treated with a H_2/O_2 mixture (1% of oxygen) show that oxygen is incorporated into the diamond surface after the MW plasma treatment. Annealing experiments on such samples, show that after UHVannealing up to 410 °C, a tunnelling between tip andthe sample is still possible, surprisingly enabling UHV-STM imaging. This allowed us to carry out STM imaging on Hterminated surfaces with atomic resolution and to monitor the surface structure of undoped (100) oriented epitaxial diamond layers for the fist time. STS and UPS measurements show that oxygen-related surface states, lying close to the valence band to which the tunneling of electrons can occur, are probably responsible for this mechanism.

Acknowledgements

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References

[1] J.A. Garrido, T. Heimbeck, M. Stutzmann, Physical Review B 71 (2005) 245310.

[2] J.P. Goss, P.R. Briddon, R. Jones, S. Sque, Diamond and Related Materials 13 (2004) 684.

[3] H. Kawarada, Surface Science Reports 26 (1996) 205.

[4] L. Ley, R. Graupner, J.B. Cui, J. Ristein, Carbon 37 (1999) 793.

[5] S. Poykko, M. Kaukonen, M.J. Puska, R.M. Nieminen, Computational Materials Science 10 (1998) 351.

[6] J. Ristein, et al., Journal of Physics-Condensed Matter 13 (2001) 8979.

[7] F. Maier, M. Riedel, B. Mantel, J. Ristein, L. Ley, Physical Review Letters 85 (2000) 3472.

[8] K. Bobrov, H. Schechter, A. Hoffman, M. Folman, Applied Surface Science 196 (2002) 173.

[9] H. Kawarada, Surface Science Reports 26 (1996) 205.

[10] J.A. Garrido, et al., Applied Physics Letters 82 (2003) 988.

[11] J.A. Garrido, et al., Physica Status Solidi A-Applied Research 193 (2002) 517.

[12] K. Bobrov, et al., Physical Review B 68 (2003) 195416.

[13] K. Bobrov, A.J. Mayne, G. Dujardin, Nature 413 (2001) 616.

[14] M. Riedel, J. Ristein, L. Ley, Physical Review B 69 (2004) 125338.

[15] M. Cannaerts, et al., Physica Status Solidi A-Applied Research 186 (2001) 235.

[16] A. Gali, J.E. Lowther, P. Deak, Journal of Physics-Condensed Matter 13 (2001) 11607.

[17] L. Diederich, O. Kuttel, P. Aebi, L. Schlapbach, Surface Science 418 (1998) 219.

[18] J.C. Zheng, X.N. Xie, A.T.S. Wee, K.P. Loh, Diamond and Related Materials 10 (2001) 500.

Figure Captions

Figure 1

XPS spectra of the samples, sample #1 hydrogenated in a H_2/O_2 mixture(a) and sample #2 hydrogenated in a pure H_2 mixture(b).

Figure 2

STM images of the hydrogenated diamond surface #1 without annealing (a), after annealing for 30 minutes at 200°C (b) and after annealing for 30 minutes at 410°C (c).

Figure 3

Schematic diagram of the band bending model of the hydrogenated diamond surface in a H_2/O_2 mixture. The symbols as the electron affinity work function χ , determined by UPS are discussed in the text.

Figure 4

The atomic resolution image of 2x1 reconstructed diamond surface of sample #1, hydrogenated in H_2/O_2 mixture and annealed in UHV at 410°C fro 30 minutes.

Figure 5

(a) The I-V characteristic of sample #2, showing an quasi-Ohmic character; (b) I-V characteristic of the hydrogenated sample #1; (c) The derivate and second derivative of the I-V characteristic of sample #1 showing a wave-like behaviour pointing to resonances with the surface states.

Figure 6

UPS spectrum of sample #1 showing the NEA of the diamond surface.

Table Captions

Table 1

The surface coverage by oxygen in several bonding configurations calculated from the XPS results. The relative amounts of oxygen and carbon atoms detected in samples by XPS are shown for both samples #1 and #2 and for a reference sample, which have been oxidized using an chemical oxidation discussed in the text. The precision for the determination of oxygen carbon and oxygen concentration is 0.3 and 0.7% respectively.

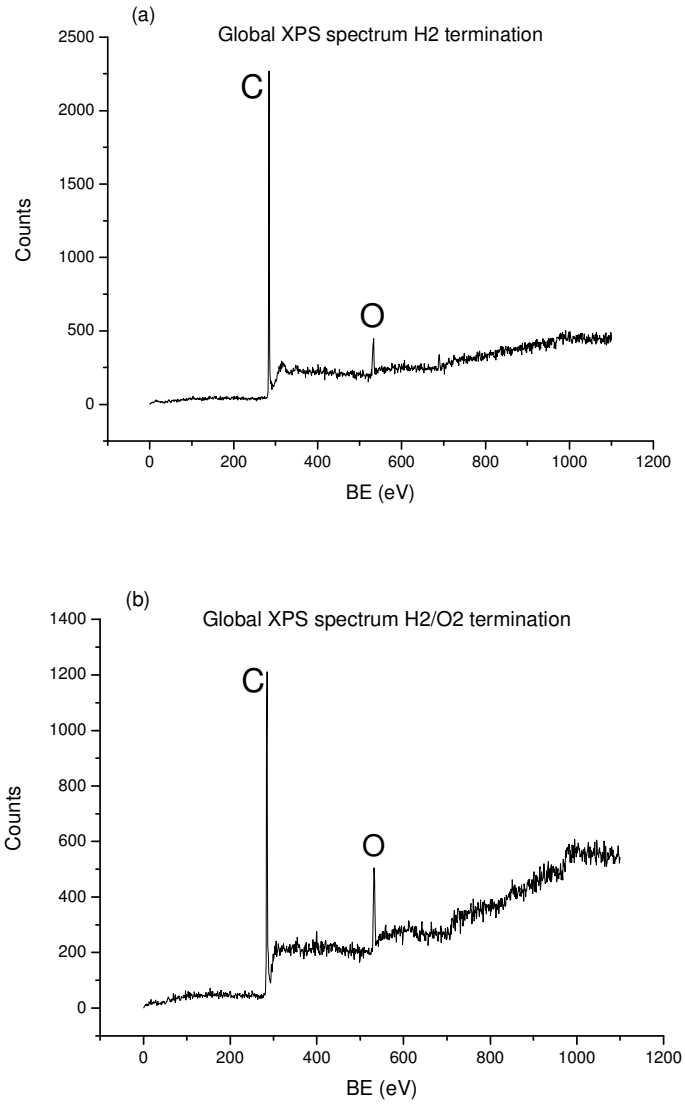
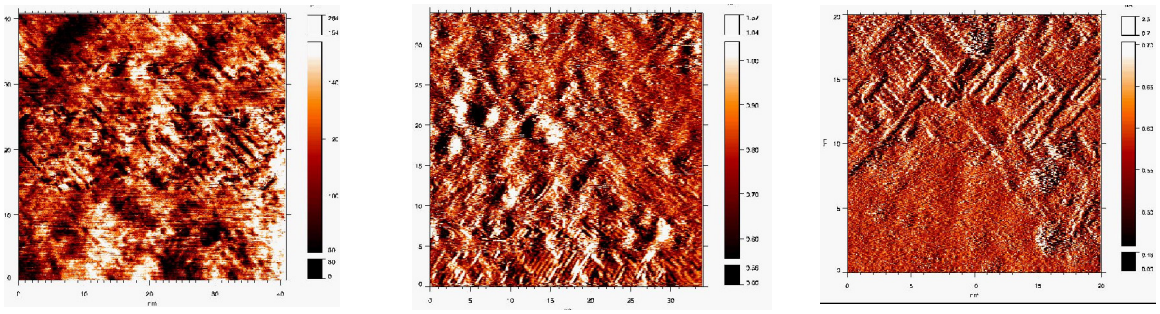

(a)
Global XPS spectrum H2 termination
C
O
Counts
BE (eV)
(b)
Global XPS spectrum H2/O2 termination
C
O
Counts
BE (eV)

Figure 1



(a) (b) (c)

Figure 2

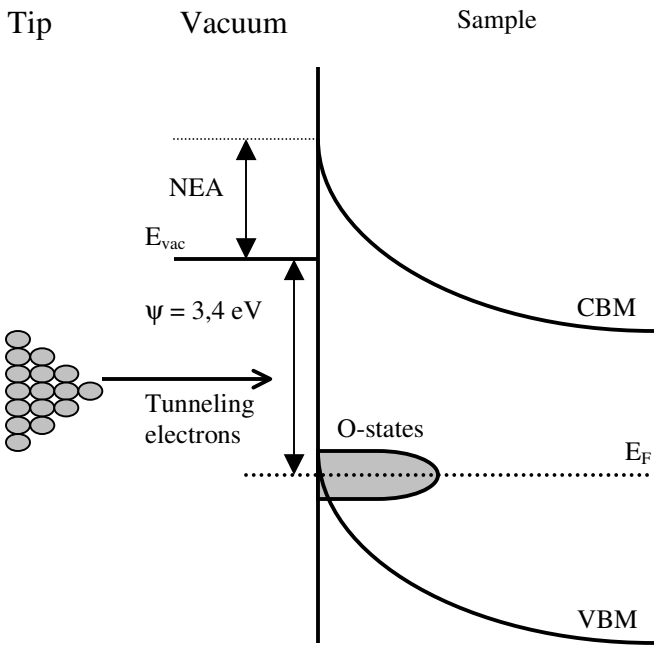


Figure 3

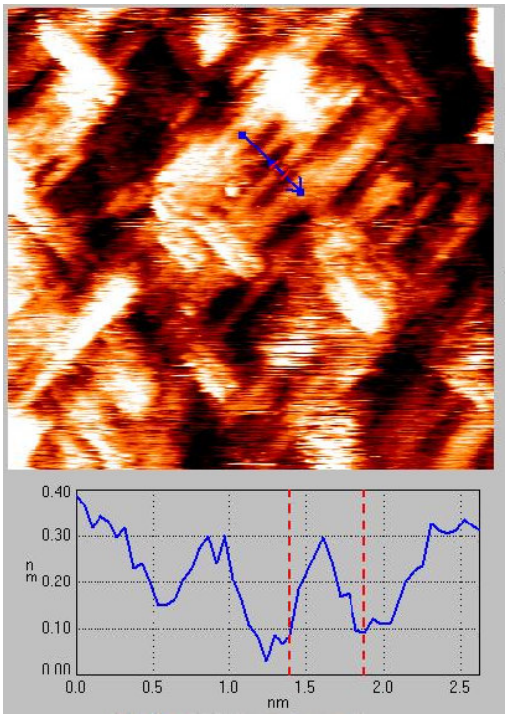


Figure 4

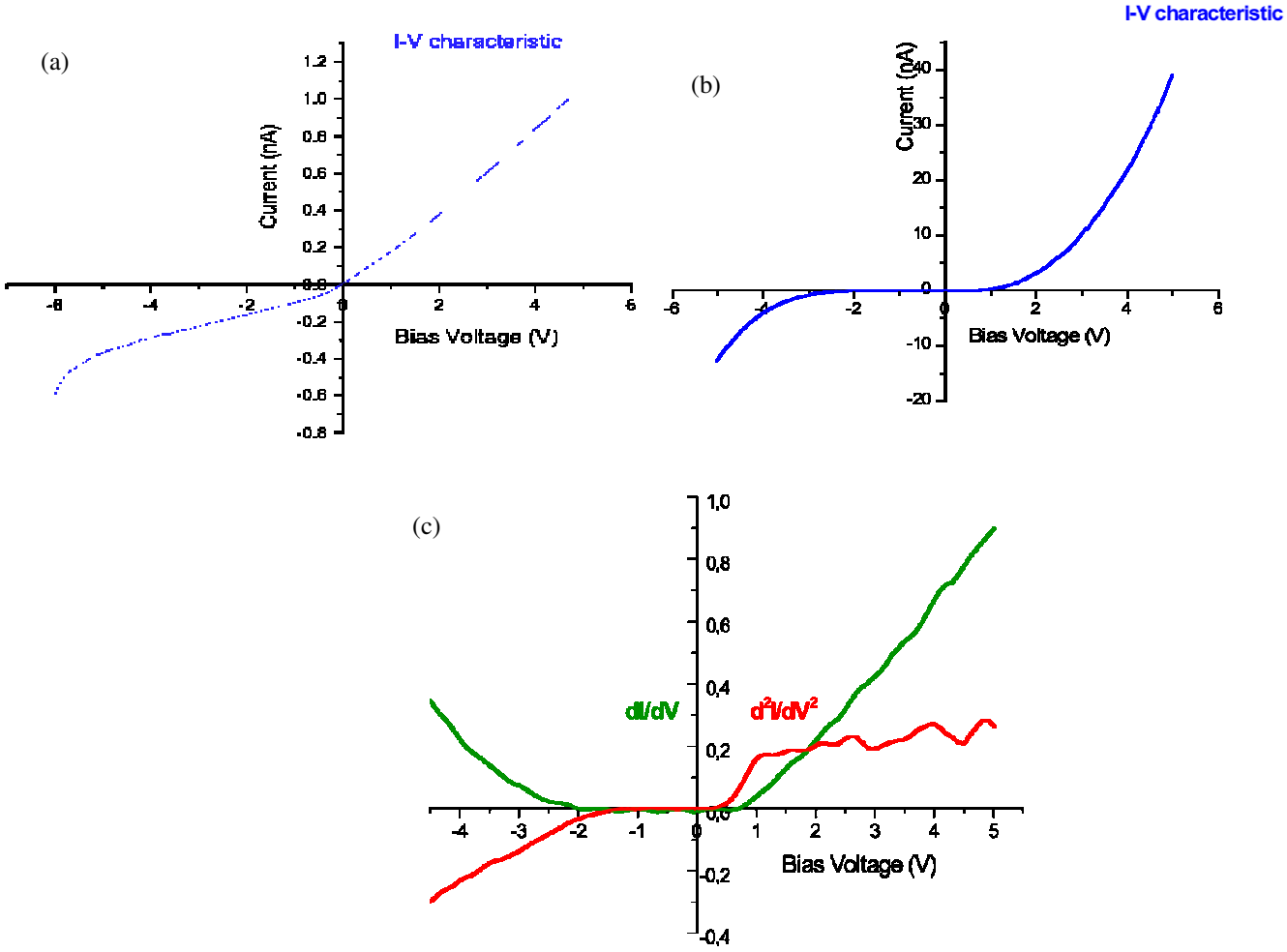

(a)
I-V characteristic
Current (nA)
Bias Voltage (V)
(b)
I-V characteristic
Current (pA)
Bias Voltage (V)
(c)
dI/dV
d²I/dV²
Bias Voltage (V)

Figure 5

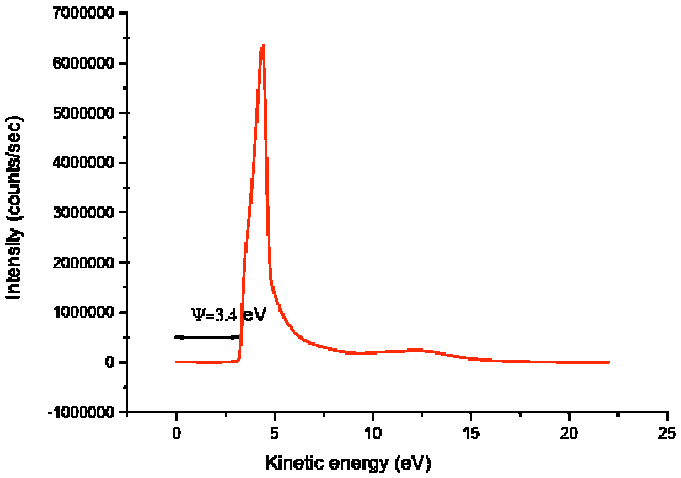

7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
Intensity (counts/sec)
Ψ=3.4 eV
0
5
10
15
20
25
Kinetic energy (eV)

Figure 6