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# Reflection anisotropy spectroscopy of the oxidized diamond (001) surface

M Schwitters<sup>1</sup>, D S Martin<sup>1</sup>, P Unsworth<sup>1</sup>, T Farrell<sup>1</sup>, J E Butler<sup>2</sup>  
and P Weightman<sup>1</sup>

<sup>1</sup> Physics Department and Surface Science Research Centre, University of Liverpool,  
Liverpool L69 7ZE, UK

<sup>2</sup> Code 6174, Naval Research Laboratories, Washington, DC 20375, USA

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## Abstract

We report reflection anisotropy spectroscopy (RAS) measurements of the oxidized (001) surface of a type IIb natural diamond. These measurements were made possible due to recent developments in diamond surface preparation. We compare RAS results from the hydrogenated, clean and oxidized C(001) surface and demonstrate that RAS is sensitive to the structural transition of the surface from the  $2 \times 1$  reconstruction of the clean surface to the  $1 \times 1$  reconstruction of the oxidized surface.

## 1. Introduction

With the recent advances in the CVD-growth of diamond and diamond processing a wide range of applications for this remarkable material become realizable. In particular, electronic devices utilizing diamond's outstanding electronic properties could soon become a commercial reality [1, 2]. Applications such as diamond Schottky-diodes have reached an advanced stage in development [3] in addition to the recent breakthroughs in diamond MESFETs—both surface-based [4] as well as bulk-transistors [5]. These devices have in common that their successful implementation relies on mastering the art of producing ultra-smooth diamond (001) surfaces. In addition to this prerequisite it is important for the realization of diamond electronics to be able to create chemically well-defined and stable diamond surfaces. Surface-conduction-based transistors rely for example on well-defined hydrogenated surfaces, while perfectly oxidized surfaces are important for surface passivation purposes for transistors and Schottky-diodes.

The various technical applications of CVD grown diamond have led to a necessary increase in diamond research including many investigations of the diamond surface. However, reproducibility of experimental observations, such as the reconstructions of the diamond surface after adsorption or desorption of hydrogen or oxygen, remains a key issue in diamond research.

Reflection anisotropy spectroscopy (RAS) [6, 7] is an optical technique that has recently been applied to the study of natural diamond surfaces [8–11]. RAS measures the difference

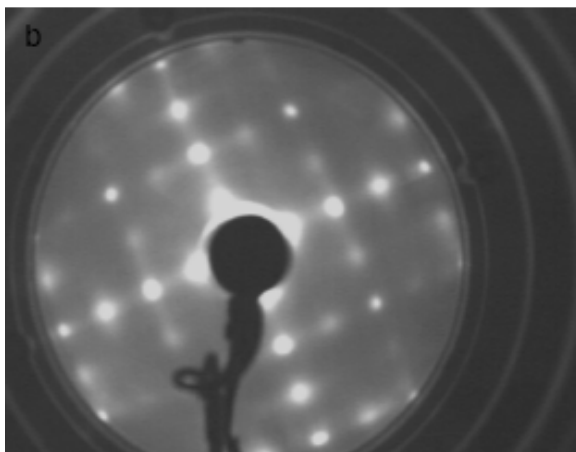
in reflection of two orthonormal light polarizations incident normal to the surface as a function of photon energy. The anisotropy,  $\Delta r$  in the normal incidence Fresnel reflection coefficients for light linearly polarized in two orthogonal directions in the surface normalized to the mean reflection  $r$  is given by:

$$Re\left(\frac{\Delta r}{r}\right) = Re\left(2\frac{r_{[110]} - r_{[1\bar{1}0]}}{r_{[110]} + r_{[1\bar{1}0]}}\right).$$

We have recently reported RAS measurements of high quality clean and hydrogen terminated diamond (001) surfaces and were able to distinguish the contributions to the RAS from surface steps and terraces [8, 9]. Comparing *ab initio* calculations with measured RAS data lead to the conclusion that surface-state excitons occur on clean diamond (001) terraces with binding energy 0.9 eV, the largest found in a semiconductor. In this work we report the results of an RAS study of the oxidized C(001) (O/C(001)) surface.

## 2. Experimental details

A type IIb natural diamond of dimensions  $8 \times 2.5 \times 4$  mm<sup>3</sup> and with (001) surfaces was obtained from De Beers. This material was chosen since boron doping, at a level of less than a part per million, makes it conducting and thus possible to characterize the surface by LEED and x-ray photoelectron spectroscopy (XPS). In this work we employ a range of processing techniques including plasma treatments to produce locally atomically smooth hydrogen terminated surfaces as a precursor to producing the O terminated surface. Details of



**Figure 1.** LEED pattern of the hydrogenated two-domain  $2 \times 1$  reconstructed C(001) surface after annealing at 500 K. The first LEED spots appear at a beam energy of 25 eV which was the energy used in exciting the LEED pattern shown in the figure.

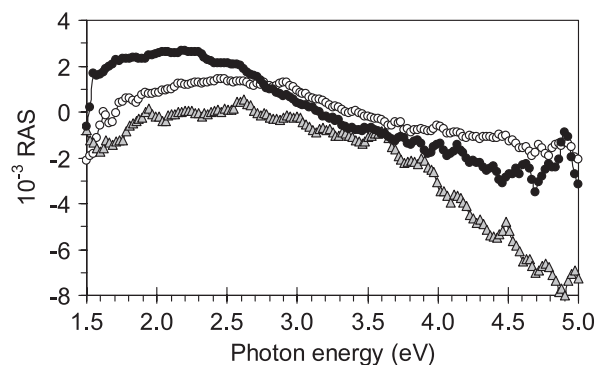
this approach have been described in detail elsewhere [8, 9, 12]. The standard surface for all experiments presented here is the hydrogenated (001) surface with a  $2^\circ$  vicinal angle oriented towards the [110] direction. The orientation was confirmed by x-ray diffraction. The RAS instrument was of the Aspnes design [6] and was mounted external to the UHV chamber, projecting and receiving light through a low strain window.

Following surface preparation at the Naval Research Laboratory (NRL) the specimens were transported to Liverpool under ethyl alcohol and then introduced into the ultrahigh vacuum (UHV) chamber of the Liverpool electron spectrometer [13] for LEED, XPS and RAS measurements. The XPS measurements were performed using a monochromated Al  $K\alpha$  source. Heat treatment of the specimens was carried out in UHV at pressures in the region of  $10^{-11}$  mbar by e-beam heating of the underside of the specimen. The sample temperature during annealing was measured with optical pyrometry and with a thermocouple positioned inside a black body cavity in the specimen in a laser-drilled hole.

Oxidation of the clean C(001) surface was achieved by thermally activated  $O_2$  created via interaction with a W filament held at around 1500 K in close proximity (less than 2 mm) to the diamond surface. The oxidation took place with the diamond specimen at room temperature and at an oxygen pressure of around  $2 \times 10^5$  mbar. Each oxidation cycle lasted 5 min. The oxygen was thermally activated to an extent where a reaction with the sample surface occurred without any of the filament material evaporating onto the diamond surface if the filament temperature was kept no higher than 1500 K.

### 3. Results

The hydrogenated C(001) diamond surface was first annealed at 500 K to remove adventitious adsorbed hydrocarbons and oxygen species. Following annealing LEED results showed a well ordered two-domain  $2 \times 1$  pattern (figure 1). XPS

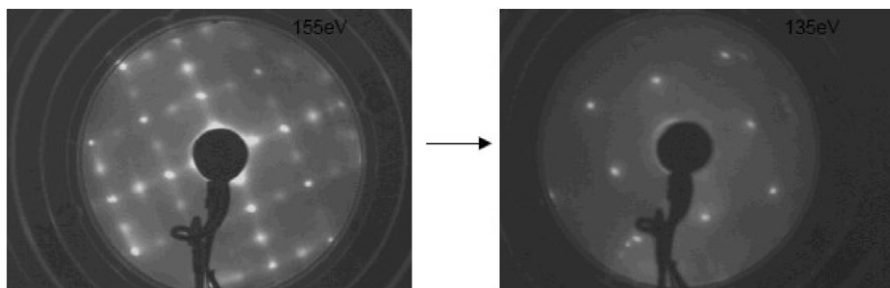


**Figure 2.** RAS spectra of the C(001):H surface (grey triangles), the clean C(001) surface (open circles) and the oxidized C(001) surface (filled circles).

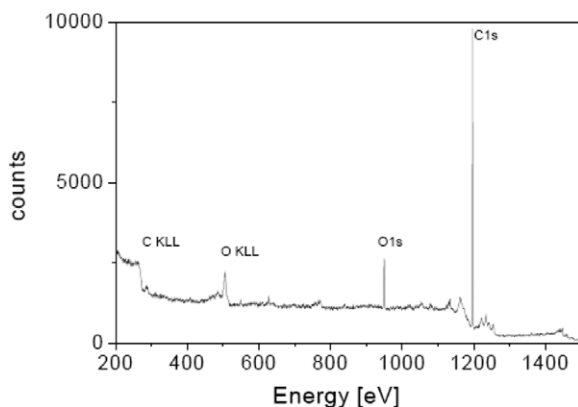
showed the single component symmetrical C 1s photoelectron line-shape characteristic of H terminated C(001)  $2 \times 1$  surfaces [14, 15]. The RAS spectrum obtained from this H terminated surface is shown in figure 2.

The surface was then heated to 1500 K to desorb the hydrogen and create a bare C(001) surface. Following cooling to near room temperature, LEED results showed the two-domain  $2 \times 1$  pattern expected from the clean surface (figure 3). The LEED patterns of the H/C(001)  $2 \times 1$  and clean C(001)  $2 \times 1$  surfaces are indistinguishable so LEED alone cannot be used to characterize the desorption of H from the H terminated surface. However heating of the H terminated specimens to 1500 K in UHV for periods of 30 min produced changes in the C 1s photoelectron line-shape that are characteristic of the C(001)  $2 \times 1$  reconstructed surface [14, 15] indicating that H has been desorbed from the H/C(001)  $2 \times 1$  surface. The C 1s photoelectron line-shape of the H/C(001)  $2 \times 1$  surface differs from that of the C(001)  $2 \times 1$  surface in that while the former is symmetrical due to the H termination of the surface C atoms producing a local surface environment similar to that of bulk C the latter shows a weak shoulder on the high kinetic energy side of the bulk C1s peak that is characteristic of the surface dimers on the C(001)  $2 \times 1$  reconstructed surface. In our experiments we found that the relative intensity of the shoulder on the C 1s line arising from the surface dimers varied in intensity following different heat treatments. This indicates incomplete desorption of H from the surface or possibly re-adsorption of H on the surfaces during cooling.

The clean C(001) surface was then oxidized following the procedure outlined in the experimental section. Previous studies investigating the atomic structure of the O/C(001)  $1 \times 1$  surface [16–18] have found that oxidation of the C(001) surface by filament-activated oxygen causes the surface atoms to form predominately C–O–C (ether-) bonds [16, 17] leading to a  $1 \times 1$ -reconstruction of the diamond surface. Our LEED and XPS results are consistent with this result for our oxidation procedure. LEED results of the oxidized C(001) surface (figure 3) confirmed the predicted sharp transition from the  $2 \times 1$ -reconstruction of the clean C(001) surface to the  $1 \times 1$ -reconstruction of the oxidized surface. XPS data showed that the oxidation of the clean C(001) surface was achieved without



**Figure 3.** LEED patterns. Left panel: the two-domain  $2 \times 1$  structure of the clean C(001) surface. Right panel: the  $1 \times 1$  structure observed for the oxidized C(001) surface.



**Figure 4.** XPS data of the oxidized C(001) surface after five consecutive oxidation cycles. The oxygen peaks in the spectrum are clearly observed and no W evaporated from the filament is detected. However very weak features from the Ta clips holding the diamond in place can be detected in the XPS spectrum. These include the  $TaM_{4,5}NN$  Auger lines and the 4p, 4d and 4f XPS lines. These features do not of course come from the diamond surface.

any detectable contamination of the sample by the W filament (figure 4).

The RAS spectra of the O/C(001)  $1 \times 1$  and clean C(001)  $1 \times 2$  surfaces are shown by the filled and open circles respectively in figure 2.

#### 4. Discussion

The RAS of the H/C(001)  $2 \times 1$   $2^\circ$  vicinal surface has been reported previously and compared with the spectra of the H/C(001)  $2 \times 1$   $0^\circ$  and  $4^\circ$  vicinal surfaces in order to deduce the spectral contributions from steps [9]. The RAS of the clean C(001)  $2 \times 1$   $2^\circ$  surface differs from that of the H/C(001)  $4^\circ$  surface as reported previously and this difference is probably caused by different step contributions [8]. Here we concentrate on the RAS of the O/C(001)  $1 \times 1$   $2^\circ$  surface. The main observation is that RAS can clearly distinguish between the three surfaces and hence has potential as a monitor of surface processing.

The RAS of the O/C(001)  $1 \times 1$   $2^\circ$  surface is dominated by a broad positive peak that stretches from 1.5 to 3 eV. It is twice as intense as, and shifted to lower energy of, the broader and weaker feature in the RAS of the clean surface. There are also indications of a positive feature between 4.5 eV and 5.0 eV

in the RAS of the O/C(001)  $1 \times 1$   $2^\circ$  surface. The negative slope in the RAS of this surface beyond 3 eV is similar to that observed on the clean surface. A larger negative signal is observed in this region from the H/C(001)  $2 \times 1$   $2^\circ$  surface and is associated with H terminated single height steps [9]. Any residual H contamination of the O/C(001) and clean surfaces would be expected to adsorb on the steps and may contribute to the RAS in this region.

Surface electronic structure data is often useful in interpreting RAS data [7]. The electronic structure of the clean C(001)- $2 \times 1$  surface has attracted experimental and theoretical interest [8, 19, 20] with evidence presented for the existence of surface states [19] and excitons [8]. Some studies of the electronic structure of the oxidized C(001) surface have been reported [21, 22]. Zheng *et al* [22] report experimental results from photoemission combined with first principle calculations and find an O-induced surface state at  $\sim 3$  eV below the Fermi edge. Liu *et al* [21] observe occupied states a few eV below the valence band arising from non-bonded O 2p orbitals. In both studies, the exact surface oxide structure, either (C–O–C) or (C=O), affects the precise details and energies of the surface states. We are not able to determine conclusively whether these O-induced states contribute to the RAS measurements. The broad RAS structure observed below 3 eV does increase for the oxidized surface (figure 2) however its broadness would imply any transitions having a large range in energy, rather than the relatively narrow RAS peaks seen on metal surfaces that are associated with transitions involving surface states [7].

#### 5. Conclusions

In this work we have extended our previous work on the RAS of the C(001):H surface to the study of the oxidized C(001) surface. Both of these surfaces play an important role in the technical application of diamond—particularly diamond electronics. It has been possible to prepare atomically smooth C(001) surfaces, a prerequisite for the controlled oxidation of these surfaces. We demonstrate that RAS is sensitive to the sharp transition from the  $2 \times 1$  reconstructed clean C(001) surface to the  $1 \times 1$  reconstructed C(001):O surface.

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