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Unexpected change in the electron affinity of diamond caused by the ultra-thin transition-metal-oxide films

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Abstract – The energetics and electronic properties of oxides of selected transition metals (Cu, Ni, Ti and Zn) adsorbed onto a diamond (001) surface are examined using density functional simulations. We find that the stoichiometric oxides of Ti and Zn exhibit large negative electronic affinities of around 3 eV, whereas the oxides Cu and Ni have a relatively small impact on the affinity. Although reactions of most metal oxides with the diamond surface are exothermic in nature, we propose that titanium, which exhibit large binding energies per metal atom in addition to a large negative electron affinity, is of particular interest for the surface coating of diamond-based electron emitters.

Introduction. – The ability to induce a negative electron affinity (NEA) on a diamond surface by suitable surface treatments has been frequently demonstrated [1–6]. In conjunction with its remarkable material properties, an NEA of diamond, where the conduction band minima lie above the vacuum level, is of particular interest for photocathode and thermionic applications, as it can significantly reduce the energetic barrier to electron emission, so that conduction-band electrons can be released into the vacuum even at low temperatures [1–9].

A widely-adopted, and perhaps the simplest approach to produce an NEA with diamond uses hydrogen surface treatments [1–5]. C–H surface bonds form a dipole layer, which helps in lowering the work function from that of carbon terminated diamond at 5 eV, to around 3 eV [1,4].

However, the reduced work function of diamond remained too high for low-temperature thermionics, and operation at elevated temperatures (above 500°C) results in the desorption of hydrogen, and a substantial increase in work function [10]. Alternative surface terminations including halogens [11,12], oxygen, [4], alkali-halides [20,21] and alkali-oxides [22,23], have also been examined, which provide some control over the electron affinity (χ). Unfortunately, most either increase the work function or are unstable at high temperatures. For example, F- and O- terminations, which are reasonably thermally stable, result in the positive χs and increase the work function [4,11], whereas CsO, which yields a low value (≈1.5 eV) of work function, is found to be highly unstable above ∼377°C [6,18,24]. Similar issues have been encountered with alkali halides [20,21].

Perhaps the best candidate currently proposed to address both NEA and thermal stability is monolayers of lithium-oxide [22,23]. However, Li is incompatible with semiconductor device fabrication processes. Hence, for an efficient electron emitter, a low work function and thermally stable diamond surface remains to be identified.

Recent theoretical and experimental studies on the deposition of transition metals (TMs) Cu, Ni, Ti, Co and Zr onto both clean and oxygenated diamond surfaces [10,15–17,19,25,26] demonstrate that TMs are very stable and influence the electronic properties significantly. Importantly, TMs are advantageous over other terminations, and particularly lithium, as they are compatible with device fabrication processes widely used for both Schottky and Ohmic contact fabrication [27,28]. These studies suggest that, in addition to the chemical nature of surface treatments, layer thickness impacts upon χ. Ul-
tra thin (the order of a monolayer) transition-metal oxide (TMO) coatings are generating a great deal of interest for thermionics, as there is a possibility of significant reduction in $\chi$ resulting from large metal-oxygen dipoles akin to those predicted for lithium oxide termination [22]. In this letter, we present the results of density functional calculations exploring the energetics and $\chi$ of a diamond (001) surface terminated by a range of stoichiometries of the oxides of selected TMs: Ti, Ni, Cu, and Zn. We demonstrate here that by careful choice of metal species, stoichiometric TMOs, in addition to producing a very large NEA, show a strong adhesion to the diamond surface, paving the way for the fabrication of thermally stable, highly efficient diamond electrodes.

Such robustness is essential for any future application in an electronic device that is compatible with mass manufacture. For example, TMO terminated diamond electrodes could be feasibility incorporated into micro-fabricated electro-mechanical devices (MEMs) that function as high efficiency ballistic power transistors. The fabrication of such devices would rely on being able to successfully deposit or bond suitable material layers on top of the diamond/TMO structure without inducing degradation in $\chi$. Li based coatings are not robust enough under typical fabrication conditions to allow for low-cost manufacture whilst TMOs (such as TiO$_2$) are already widely used in MEMs type structures.

Methodology. – Density-functional calculations are performed within the local-density approximation (LDA) [29] using the AIMPRO code [30–32]. Atoms are modeled using norm-conserving, separable pseudo-potentials [33], and Kohn-Sham eigen-functions are expended using atom-centered Gaussian basis sets [34]: all species are associated with independent sets of $s$- and $p$-functions of four widths, and either two (oxygen) or four (all other species) sets of $d$-functions, amounting to either 28 or 40 independent basis-functions per atom. Matrix elements of the Hamiltonian are determined using a plane-wave expansion of the density and Kohn-Sham potential [35] with a cutoff of 175 Hartree, resulting in convergence of the total energy with respect to the expansion of the charge-density to within around 10 meV. Using this approach, the diamond lattice-constant is 3.53 Å, just 1% less than experiments, and the calculated indirect band gap is 4.20 eV, consistent with comparable plane-wave calculations [36]. The qualitative and quantitative details regarding surface calculations have been published previously [11, 14]. Surfaces are simulated using a 14-layer, (001)-oriented slab, separated by a minimum of 15 Å of vacuum. In-plane surface lattice vectors are $n[110]a_0/2$ and $m[110]a_0/2$, $n$ and $m$ being integers.

Structures are optimized using a conjugate-gradients scheme, with the optimized structures having forces on atoms $<10^{-3}$ atomic units, and the final structural optimization step is required to result in a reduction in the total energy of less than $10^{-5}$ Hartrees. The Brillouin zone is sampled using uniform Monkhorst-Pack sampling meshes [37]. The initial sampling for a $1 \times 1$ surface cross-section is $8 \times 8$ and for calculations where the primitive surface cells are repeated, the sampling is reduced to maintain the sampling density.

In line with the standard practice [38–40], $\chi$ is calculated by finding the electrostatic potential (EP) and associated vacuum reference level as a function of position through the slab into the vacuum, and aligning this to the corresponding EP variation in the bulk diamond, which is equivalent to the position of valence band maxima. It is worth mentioning here that the experimental value of 5.47 eV of energy bandgap is added to the position of valence band maxima to accurately predict the position of conduction band minima of bulk diamond in simulations. Using this approach we have accurately predicted the electron affinities of some common surface terminations, such as $-\text{H} (\approx 1.9 \text{ eV})$ and $-\text{F} (\approx 2.1 \text{ eV})$, which are in good agreement with experiments ($\text{H}$ at $-1.3 \text{ eV}$ [1] and $\text{F}$ at 2.6 eV [42]). For H-termination, the difference between the current and previous calculations is less than 0.1 eV [39, 40].

The adsorption energy ($E_{\text{ads}}$) per atom for each equilibrium structure is calculated [11, 14, 22, 25] as

$$E_{\text{ads}} = \frac{1}{n} \left( E_{\text{tot}} - E_{\text{ox}} - n\mu_X \right),$$

where $E_{\text{tot}}$ is the total energy of the $a \times b$ diamond slab terminated by both TM and oxygen atoms, $E_{\text{ox}}$ is the total energy of the $a \times b$ oxygen-terminated diamond slab, $\mu_X$ is the energy of a free metal atom, and $n$ is the total number of metal atoms in the $a \times b$ slab. The method used to determine $\mu_X$ are detailed elsewhere [14], but in brief the difficulty in reliably obtaining atomic energies is avoided calculating energies of solids and determining atomic energies using experimental cohesive energies. We have assessed the impact of functional by calculating properties of selected surface using the generalized gradient approximation (GGA) [41]. In GGA calculations, $\chi$ is found to deviate from the LDA values by less than 10%, and $E_{\text{ads}}$ remain unchanged to within 10s of meV.

Results and Discussion. – We now examine the terminated diamond surfaces. It is understood that on the (001)-diamond surface, oxygen binds in an ether form, whereas hydrogen termination takes the form of a structural reconstruction akin to that seen in H-termination. In this case oxygen in the negative oxidation state is thought to be a $\text{H}$ substituent, rather than a divalent. Combining the $\text{H}$ oxidation state of the surface oxygen with the native oxidation state of each TM, it is possible to reduce the otherwise large
number of possible surface arrangements for the various monolayers of TMOs: this results in 25%, 50% and 100% of the surface site coverage for MOs that normally adopt $\text{M}_2\text{O}_3$, MO and MO$_2$ stoichiometries, respectively. For example, as shown schematically in Fig. 1, each Ti$^{4+}$ and Zn$^{2+}$ ion in the stoichiometric films is balanced by four and two oxygen atoms, respectively.

A wide range of possible surface geometries for each stoichiometry were examined, including those where the TMs are bonded directly to the diamond, leading to a C–TM–O surface termination. In all cases examined, structures where the oxygen atoms act as linkers between the diamond and the TM were energetically favored, and it is only such arrangements that are discussed in the remainder of this letter.

The impact of adopting the appropriate stoichiometries can be seen on $E_{\text{ads}}$ listed in Table 1; we indeed find the most stable configurations of Ti, Ni, and Zn occur for ratios of 1:4, 1:2, and 1:2, respectively. The equilibrium configurations corresponding to oxides of zinc and titanium are shown schematically in Fig. 2. In the case of Cu we note that $E_{\text{ads}}$ for the ratio 1:1 is slightly lower than that of the ratio 1:2. These correspond to the cupric and cuprous oxides. The enthalpy of formation of cuprous oxide ($\text{Cu}_2\text{O}$, $-169$ kJ/mol) is slightly greater than that of cupric oxide ($\text{CuO}$, $-157$ kJ/mol), with the differences in formation enthalpy agreeing reasonably well with the corresponding structures on diamond, $(\Delta H \approx 0.1 \text{ eV per Cu atom, and } \Delta E_{\text{ads}} \approx 0.06 \text{ eV})$.

(a) Titanium oxide

(b) Zinc oxide

Fig. 2: Perspective views of the diamond surface with adsorbed oxides of (a) Ti and (b) Zn. Black, red, gray, and brown spheres represent C, O, Ti, and Zn atoms, respectively.

The values for $E_{\text{ads}}$ listed in Table 1 are broadly comparable with those found recently for the same TM species on the oxygen-free (001)-diamond surface [13, 14], confirming that TMs are strongly attached to an oxygen-terminated diamond. Since in most of cases, adsorption of TMs onto an oxygenated diamond surface is exothermic, one may expect better thermal stability from metal oxides at elevated temperatures in comparison to commonly used surface terminations, such as H, and other alkali halides and oxides.

As an example, in the case of the most energetically favorable stoichiometry, 1:4, of titanium oxide, to extract a Ti atom from an oxygenated diamond surface and brings it in the gaseous form, one will have to provide thermal energy equivalent to 7.60 eV. Alternatively, one might envisage the desorption of an oxide species, leaving behind a clean diamond surface. We estimate for the titanium-oxide case, release of a TiO$_2$ unit from the surface would require around 7 eV, again suggestive of a high thermal stability, although a detailed kinetic model would be required to fully explore this question. The relatively weak binding corresponding to 1:4 of Cu, Ni, and Zn suggest that at very low coverages, island formation may occur and mixed termination with both TMO islands and pure C-O surfaces are likely to be achieved in practice.

The periodicity of the underlying diamond reconstruction is found to have a relatively weak impact upon either $E_{\text{ads}}$ or $\chi$. As an example, for stoichiometric ZnO, two isomers are shown in Fig. 3. The ground state periodicity is indicated in Table 1. The most stable stoichiometries of TMOs, particularly, oxides of Ti and Zn, exhibit large NEAs of around 3.1 eV, significantly higher than H-termination ($\chi_{\text{exp}}$ is 1.3 eV and $\chi_{\text{theo}}$ is 1.96 eV) [1, 4, 11, 39, 40], but slightly smaller than 3.89 eV predicted for LiO ($\chi_{\text{exp}}$ for LiO is not known) [22, 23]. We note that the predicted sign of the electron affinity is consistent with a previous study [17], which reports a NEA for a TiO$2\times1$-(111) diamond surface.

The Pauling electronegativities of Ti, Zn, Cu, and Ni are 1.54, 1.65, 1.90, and 1.91, respectively, indicating that for stoichiometric films the bond-polarity of for Ti and Zn should exceed those of Cu and Ni. This picture is supported by Mulliken population analysis. In addition, examination of rumpling [43] is also helpful in semi-quantitatively interpreting $\chi$. The electronegativities of

Fig. 3: Top views of 2 × 1 (left) and 2 × 2 (right) geometries of a ZnO terminated diamond surface. The surface dimers are shown in green.

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Cu and Ni are very close, but the rumpling of CuO exceeds that of NiO, consistent with the more negative $\chi$ (Table 1) for CuO termination. Although Zn is less electropositive than Ti, the greater rumpling of ZnO termination leads to Zn and Ti terminations having very similar NEAs. The difference between the Ni and Cu cases highlights the necessity to not only take the nuclear arrangement into account when considering the origin and magnitude of NEAs, but also an accurate simulation of the electronic spatial arrangement.

Akin to a H-terminated diamond, the resultant electric field from the positively charged metal ion layer to the negatively charged oxygen layer of these surface dipoles results in a reduction in $\chi$ relative to an unterminated surface. An excess of metal generally reduces the magnitude of charge transfer, rendering $\chi$ less negative. Indeed, we find that that for all four TMs studied, metal bi-layers result in a positive $\chi$, consistent with the experimental studies, where relatively thick coatings of Cu, Ni, Ti Zr and Co all yield [10,15–19] positive values for $\chi$.

The effect of metal adsorption on the band structure of a purely oxygen-terminated diamond surface is shown in Fig. 4. The highly polar metal-oxygen bonds shift the band structures upwards by around 5.5 eV relative to that of oxygen termination. Also evident is that the TM-terminated surfaces are found to be non-metallic, although there are surface states introduced into the diamond band-gap, which depend upon the chemical nature of system. Wave-function analysis indicates that the unoccupied states around the vacuum level in Figs. 4(b) and (c) are oxide related, originating from a linear combination of $p$ and $d$-like orbitals centred on O and the TMs, respectively.

It is instructive to assess the bonding in the mono-
Fig. 4: Band structures in the vicinity of the band-gap along high-symmetry directions in the Brillouin-zone for the (001) diamond surfaces terminated with (a) oxygen, (b) titanium oxide (O:Ti is 4:1) and (c) zinc oxide (O:Zn is 2:1). Red and blue lines correspond to occupied and empty states. In each case the zero on the energy scale vacuum. The cross section area of all three slabs is (2 × 2).

layer surface coverage by comparing the calculated surface bond-lengths (Table 1) with suitable reference materials. In the monolayer systems, TM–O bond lengths are within 6% of the average TM-O bond lengths in the corresponding bulk metal-oxides [44, 45], but close to the values at a pure metal-oxide surface [46]. The average C–O bond length is around 9% shorter than the calculated value for ether-terminated diamond (001)-surface [40], but within 1% of the values typical for C–O− bonds [47]. The bond-lengths are therefore entirely consistent with expectations for the context.

Although the surface C–C reconstruction increases relative to that of a comparable fully hydrogenated surface, we find that the underlying 2 × 1 and 2 × 2-reconstruction are retained for all stoichiometries, for all TMOs studied. The surface C–C bond lengths on 2 × 2 geometry are relatively larger than those on 2 × 1 geometry. We note that thick TMO films are likely to have more complex issues arising from commensurability of the diamond surface and oxide structures, but for the ultra-thin films examined in this study, there is no evidence to suggest a significant role for strain.

Our findings show that a careful control is necessary while depositing ultra-thin TMO layers on diamond, as uncontrolled deposition may well result in stoichiometries that reduce the desired impact upon the χ. Selective deposition of such ultra thin TMOs films is likely to be technologically challenging. However, the use of atomic layer deposition and scanning probe based lithography for atomic scale patterning of TMs on diamond surface may offer a laboratory solution to test the impact of the ultra-thin TMO layers.

Conclusion. – In conclusion, we have examined the energetics and χ of diamond (001) surfaces terminated by selected TMO monolayers. We find that for a correct stoichiometry, ultra thin coatings of TMOs, particularly the oxides of Ti and Zn, cause a large negative shift of around 3.6 eV in the electron affinity. Since the reactions of TMs with oxygenated diamond are highly exothermic, in addition to excellent chemical stability, a better thermal stability at elevated temperatures in comparison to H and CsO can be obtained. We note in particular that Ti also has the advantage over Cs- and Li-based χ modification in that it is already commonly used in semiconductor processing. We therefore propose that in the regime of ultra thin films, Ti based TMOs are ideal for the surface coatings of diamond-based electron emitters.

We have included the evaluation of four TMOs in this letter, with titanium representing the strongest candidate for a thermally stable NEA termination for diamond surfaces. However, based upon the relationship between TM electronegativities and the resultant χ, combined with knowledge of the thermal stability of other TMOs, allows for further predictions. For example, Sc, Zr and V are also of particular interest, as these have favorable electronegativities and readily form thermally stable oxides. Analysis of such alternatives is ongoing, in tandem with experimental determination of the impact of such treatments upon electron emission.

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