

Role of HOPG density of empty electronic states above vacuum on electron emission spectra induced by ions and UV photons



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ABSTRACT

We present results of secondary electron emission (SEE) induced by UV photons and low energy He ions interacting with a pristine and ion damaged surface of highly-oriented pyrolytic graphite (HOPG). A critical examination of the changes in the SEE spectra produced by the radiation damage allows us to identify the origin of the different features of the SEE spectra. In this way, we conclude that the low energy peak at ~3 eV is strongly determined by the structure of the (empty) HOPG density of states above vacuum level. In contrast the high-energy structure at ~14 eV could not be explained by such an argument but rather by exciton autoionization.

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1. Introduction

Experimental probing of unoccupied conduction bands near surfaces provides a strong test of theories, which find difficulties in accounting for the breaking of symmetry and periodicity but by the finite lifetime of electrons and holes. The latter is of particular importance in a material such as carbon, and can be tested using its multiple allotropic forms. In a previous publication [1] we reported a study of electron emission from highly-oriented pyrolytic graphite (HOPG) induced by 1–5 keV He⁺ and Li⁺ ions. The energy spectra of emitted electrons, N(E), obtained over a wide range of polar and azimuthal angles showed a broad peak at E = 10–20 eV for He⁺, but not for Li⁺ projectiles. A theoretical analysis explained the observations as due to electron promotion in He–C (but not in Li–C) collisions leading to the formation of a transient electron–hole pair that decayed into vacuum by autoionization. The results did not follow the usual correlation with structure in the final density of states (f-DOS) of conduction-band electrons that helped interpret previous studies of secondary electron emission (SEE) by electron impact [2,3] and inverse photoemission. The role of structure in the f-DOS has been discussed in the past regarding also photoelectron (UPS) [4,5], inverse photoemission (IPES) [6], and metastable de-excitation [7] electron spectroscopies.

Recent studies of SEE from graphene [8] have returned to the question of whether peaks in the energy distribution of secondary electrons can be explained by invoking only structure in the initially empty f-DOS. Since SEE results from multiple electron collisions where, unlike

photoelectron excitation, fractional energy transfers are possible, it is tacitly assumed that structure in the initial valence-band DOS is washed out and that only the f-DOS modulates the energy distribution of secondary electron emission.

We have now improved and expanded these studies by using an electron energy analyzer that has a narrow angle of collection around the surface normal of an HOPG sample. We used as projectiles 2–5 keV He⁺, 21.2 eV (He-I) and 40.8 eV (He-II) ultraviolet photons incident on either pristine or ion-damaged surfaces. In addition, we altered the surface electronic structure by damaging the surface with 5 keV helium ions, and studied the resulting changes in the energy spectra of ejected electrons.

2. Experimental methods

The experiments were done in a UHV (base pressure in the 10^{−10} Torr range) UNI-SPECS system equipped with a 150 mm mean radius hemispherical analyzer, an electron gun, a UV He gas discharge lamp, and a differentially-pumped mass-analyzed ion gun. In the experimental setup the sample was normal to the entrance axis of the analyzer and the incidence angle of the ion beam with respect to the sample normal was 55°.

The HOPG sample was introduced in vacuum immediately after cleavage and heated by rear electron bombardment to 1100 K for several minutes. After this treatment, no contamination was observed by Auger electron spectroscopy (AES). Nevertheless, since SEE is quite more sensitive to contamination than AES, the ultimate check of the surface state was the repeatability of the electron energy spectra after annealing. The total ion fluence was kept below the threshold for

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damage that causes changes in either plasmon energy or work function. In addition we measured, at each ion energy, several electron spectra at the same spot and from different surface spots to detect any influence of damage. The sample was electrically biased at -2 V to ensure the acquisition of the complete energy spectra.

3. Results and discussion

Fig. 1 shows electron energy distributions $N(E)$ induced by 2–5 keV He^+ ions, taken with the SPEC's hemispherical analyzer. To magnify the effects we want to discuss, we depict the results taken in the Fixed Retarding Ratio (FRR) mode of the analyzer, i.e. transmission of the analyzer proportional to electron energy. In this way, the weight of more energetic electrons is enhanced. Additionally, we normalize the spectra to the total area, so the relative weights of each contribution are highlighted. We observe three peaks that present different energy dependence. Two of them are located in the energy range below 5 eV, and the third at larger energies (≈ 14 eV). With increasing ion energy, the lowest energy peak becomes subdued, while the more energetic structure increases its weight.

One is usually tempted to assign the presence of peaks in ion induced electron emission to potential processes like Auger neutralization (AN) [9,10], or indirect kinetically excited processes like plasmon de-excitation [11]. While the low energy structure is presented here for the first time, we have already analyzed the possible origin of the more energetic peak. In a previous publication [1] we concluded that neither Auger, nor plasmon de-excitations are responsible, suggesting a new mechanism based on the autoionization of an exciton, whose results are depicted in Fig. 1, as a continuous curve [1].

We will briefly recall our arguments. While it has been experimentally shown that plasmon de-excitation does not produce visible electron emission in HOPG [3], the AN interpretation is allowed by a simple energetic analysis i.e., electrons have a maximum emission energy at the ionization potential of He minus twice the work function value (Φ) ($24.6 \text{ eV} - 2 \times 4.7 \text{ eV} = 13.2 \text{ eV}$) plus a small kinematic broadening of a few eV. The vertical lines in Fig. 1 show the maximum energy for AN neglecting broadening. Two different facts are against this mechanism as responsible of the high-energy peak in electron emission. First, the dependence of the peak intensity with ion energy is not only larger than that expected for AN, but it also has the inverse sense, i.e. the importance of AN is known to decrease with ion velocity due to the decreasing interaction time with the surface [8,9]. Second, a recent theoretical study [12] has shown that resonant neutralization (RN) to $n = 2$ states is by far the main neutralization mechanism for He^+ in HOPG, rather than AN. Although RN does not produce electron

emission, the excited states (He-1s2s , $1s2p$) formed by RN may decay by Auger de-excitation (AD) generating secondary electrons. The energetic of this decaying process is more complicated than our simple estimation for AN. For thermal $\text{He } 2^3\text{S}$ atoms on graphite, AD produces electron spectra with energies up to 16 eV, with a sharp peak at 3 eV, a broad peak at ~ 8 eV and a broad, shallow shoulder at ~ 12 eV [13]. The latter two peaks shifted when using excited atoms of a different excitation energy and therefore can be ascribed to AD. However, although the population of different excited He states in RN depends on projectile velocity, producing a kinematic change in the details of the ion trajectory [14], the overall dependence of the intensity of the AD peaks should, as in AN, fall with increasing velocity as interaction times for RN and subsequent AD are shortened.

In contrast with the potential SEE mechanisms (AN and RN + AD), kinetic electron emission produces an electron yield that increases roughly linearly with energy above ~ 1 keV. This process results from direct binary collisions between He and target electrons and through promotion of electrons in the transient quasi-molecule formed in the collision to states in the continuum [9]. Its signature is a strong ion energy dependence of the electron yield above threshold, which occurs when it is possible to achieve a minimum distance of closest approach required for promotion. Although none of these kinetic excitation mechanisms is expected to give structure in $N(E)$, peaks could occur if the population of final states is determined by f-DOS structure. This is the point we are trying to elucidate in this work.

To gain insight on the influence of the structure of f-DOS on these experiments, we measured ultraviolet photoelectron spectra (UPS) at two different photon energies allowing us to perform the separation of the structure in the initial and final density of states [5]. UPS gives a convolution of densities of initial states, transition probabilities, and density of final states. The spectra are usually plotted as a function of binding energy $\text{BE} = E_{\text{ph}} - (E + \Phi)$, where E is the kinetic energy measured by the analyzer of work function Φ . Comparison of spectra for two photon energies, on a common binding energy plot, shows structure in the density of initial states where peaks match. In contrast, when peaks match in the kinetic energy plot, they indicate structure in final states, assuming a transition probability varying smoothly with energy.

Fig. 2 shows spectra collected normal to the surface with He-I (21.2 eV) and He-II (40.8 eV) photons. Our UPS results are in good agreement with previous works, mainly those published by Takahashi et al. [5], for emission along the surface normal, and Marchand et al. [4]. In particular, the assignment by Marchand et al. of the 13.5 eV binding energy feature (peak 1) to a well defined final state, based on its energy dependence on the UV photon energy, agrees with our argument based on the differences observed among He-I and He-II spectra. In contrast, the similar position of peaks 2–4 in the He-I and He-II spectra shows that they originate from the occupied DOS.

After establishing the different origin of UPS peaks it is interesting to compare in a direct way the UPS kinetic energy spectra to those induced by incident ions. This is done in Fig. 3.

The evolution of the low energy structure shown in Fig. 1, the empty DOS structure revealed in Fig. 2, and the comparison depicted in Fig. 3 give us useful evidence on the influence of f-DOS in our experiments of SEE. Thus, we have a broad SEE peak at ~ 1 eV formed by true secondary electrons (originated by the electron cascade and Auger neutralization), and a sharp peak at ~ 3 eV reflecting structure in the f-DOS. We note that the double peak structure was not observed in our previous work due to the broadening produced by the angular integration of our (Cylindrical Mirror) analyzer. As the ion energy increases, the SEE peak becomes subdued and its maximum shifts to larger energies due to the presence of the sharp peak.

So far, we discussed the mechanisms involved in the low energy electron structure of ion induced electron emission by He on HOPG. We now turn into the question on the origin of the high energy peak. To go further in the identification of final state effects, we subjected

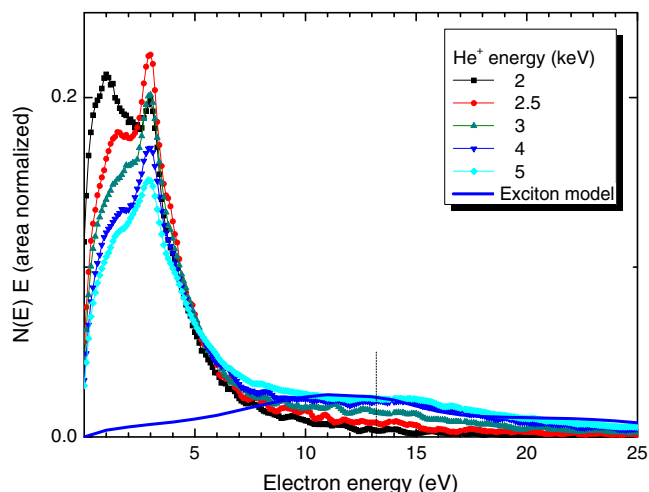


Fig. 1. He^+ ion induced electron emission spectra from HOPG normalized to total area. Continuous line represents the autoionization model (see text).

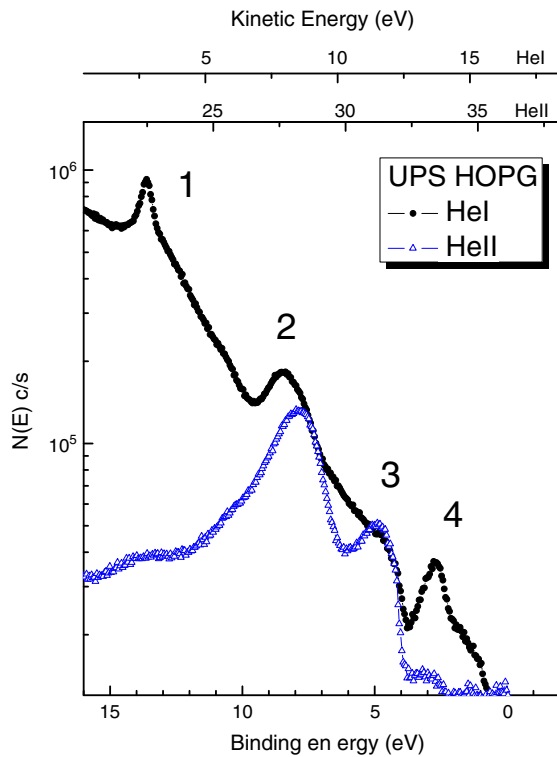


Fig. 2. UPS results for HOPG and He-I and He-II UV lines. The horizontal scales show binding and kinetic energies for both cases. Peaks are labeled for future discussion.

the samples to damage by irradiation with 5 keV He^+ ions. Previous studies [15] have shown that N^+ and Ne^+ ion irradiation affects the occupied DOS by introducing new states near the Fermi level (where DOS goes to zero in undamaged graphite), and by broadening the valence band structure with small changes in peak positions. The effect of damage in final states has been seen in the smearing of diffraction effects (UPS peak at 13.5 eV binding energy). Similar effects with neutron irradiation [16] show that the spectral changes are due to damage and not to He implantation.

Fig. 4 shows several interesting effects in the UPS spectra evolution under ion bombardment. The appearance of occupied states at the Fermi energy is clearly shown in the inset. The effect of damage is the lowering and broadening of peak 1, corresponding to empty DOS states

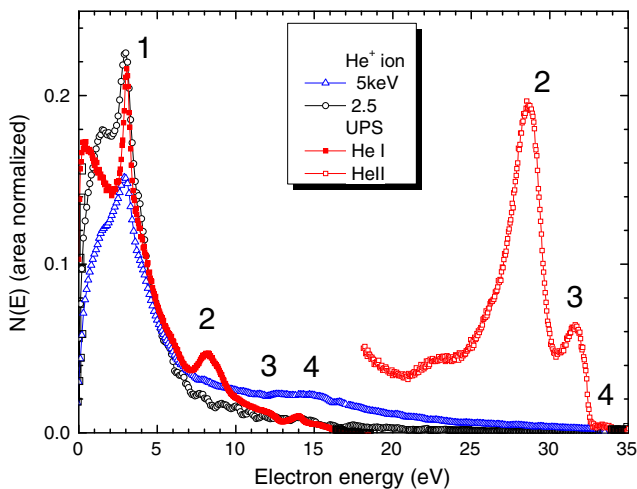


Fig. 3. Kinetic energy spectra of electrons induced by 5 and 2.5 keV He^+ ions and ultraviolet photons. The numbers on the peaks of the UPS spectra refer to the structures labeled in Fig. 2. All spectra are normalized to total area.

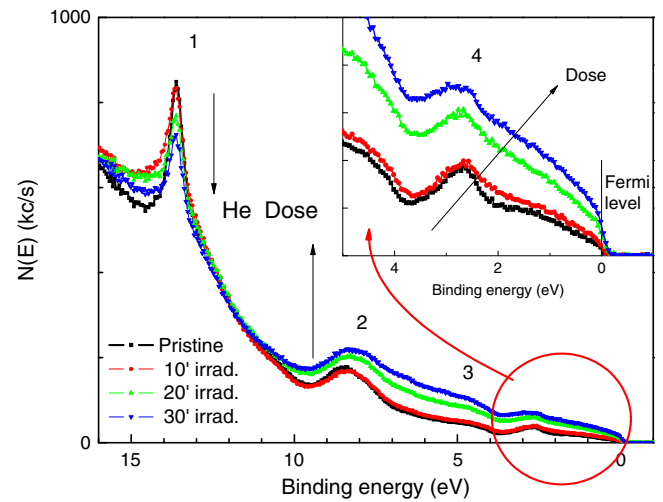


Fig. 4. Binding energy spectra showing the evolution of empty and filled DOS (as discussed in text) with time of irradiation by 5 keV He^+ ion bombardment, measured with UPS (He I).

above the vacuum level (KE \sim 3 eV, BE \sim 13.5 eV), and the attenuation, broadening and shift of peaks 2, 3, and 4. Disorder also enhances the DOS near the Fermi level ($E = 16.5$ eV) by removing the near-gap caused by the lattice periodicity and also a large increase in intensity at lower binding energies down to 10 eV.

Fig. 5 shows the evolution of 5 keV He^+ induced $N(E)$ with damage by He ion bombardment. There are at least two simple correlations when comparing UPS with particle induced spectra: the decrease and the broadening of the low energy SEE peak, consistent with that of UPS peak 1, assigned to changes in the empty DOS over the vacuum level.

Besides the attenuation of the sharp 2.7 eV due to the f-DOS, the evolution with damage of the higher energy electrons induced by ions, in particular the 14 eV peak, does not follow at all that of the DOS shown by UPS peak. The effect of damage is the disappearance of the valley between 5 and 13 eV, while affecting only slightly the spectra at and above the peak at 14 eV. There is no indication of UPS peaks 2 and 3 that should appear at kinetic energies of 8.2 and 11.7 eV. Peak 4, at a kinetic energy of 13.7 eV, cannot be linked with the \sim 14 eV peak excited by ions since it is much narrower and appears in all UPS spectra, even those corresponding to large ion doses while the ion-induced peak disappears.

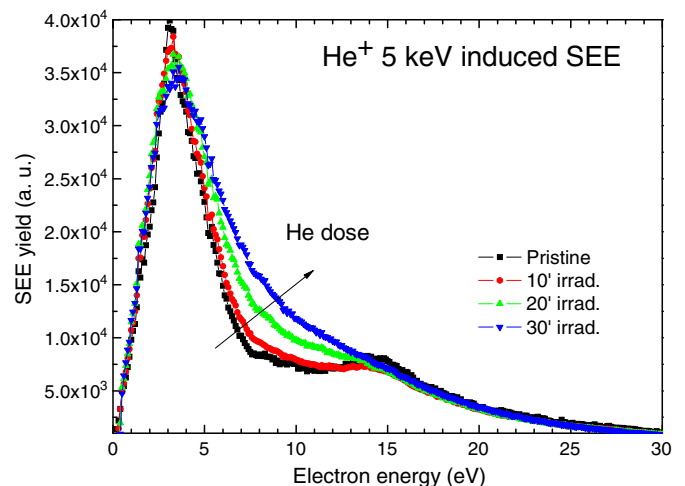


Fig. 5. Electron energy spectra induced by 5 keV He^+ for HOPG surfaces subject to increasing damage as in Fig. 4.

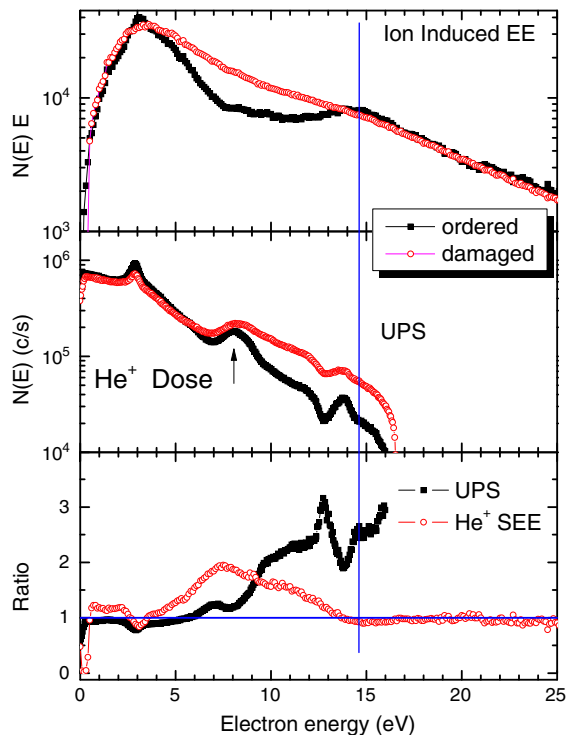


Fig. 6. Comparison of electron energy spectra obtained with He-I UV and 5 keV He^+ from pristine and heavily damaged HOPG. The vertical lines show the position of the high-energy peak.

In Fig. 6 we show the effect of damage in a more quantitative way, by comparing the ratio among electron emission coming from heavily damaged and pristine HOPG. The differences between ion and photon-excited electron spectra ratios shown in Fig. 6 (bottom panel) suggest that the effect of damage is different in both cases, and therefore changes in electron energy distributions cannot be attributed only to changes in the density of unoccupied states, which is common to both UV and particle excitation.

Spectral changes due to ion irradiation of HOPG can be understood from the lattice disorder caused by collision-induced atomic displacements, which alters the crystal periodicity near the surface. Radiation induced disorder introduces new electronic states in the conduction band due to the destruction of interference effects by scattering. This decoherence tends to erase the band gap 5–16 eV above the vacuum level as calculated [17] and observed in low-energy electron transmission [18] and in angle-resolved UPS [19] in the direction normal to the surface, as used in our experiments. This effect is clearly seen in the UPS ratio, and it is also apparent in the 3–13 eV region of the ion-induced electron emission.

The prominent ~14 eV peak excited by ions is above the band-gap region and can be explained by the exciton autoionization proposed

previously [1]. The decrease in intensity with ion irradiation suggests a decrease in exciton lifetime due to coupling with configurations allowed by disorder by increasing coupling to layers below the surface.

4. Conclusions

We have presented results of SEE induced by UV photons and low energy He ions interacting with an HOPG surface. The evolution of the low energy (<5 eV) structure of SEE peaks with ion energy clearly shows the modulation of the empty DOS, in the low energy electron emission process. This modulation is additionally confirmed by the examination of the changes in the SEE spectra induced by the radiation damage. On the other hand, the high-energy structure (at ~14 eV) does not appear to be related to structure in the f-DOS and arises from a different mechanism, likely exciton autoionization. The additional contribution of Auger de-excitation following resonant neutralization to excited states of He [12] is unlikely but cannot be determined at this point without further experiments and theoretical studies.

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