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First-principles evaluation of the secondary electron yield ($\gamma^N$) from polyethylene surface

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Abstract

We have performed first-principles calculations (DFT) to estimate the secondary emission yield (SEY) through Auger neutralization mechanism ($\gamma^N$) related to the impact of a series of ions on a polyethylene surface. We have considered many relevant ionic species, such as Ar$,^+$, which is often used as a benchmark. Our main goal is to study dielectric surfaces but, to check the validity of our approach, we have also considered some metallic surfaces (Al, Cu, Cu:N, Cu:O and CuO) on which some more experimental data can be found. On the contrary, very few references are available regarding the Auger neutralization on insulating materials and, in particular, on polyethylene.

The SEY outcomes for metals have basically reproduced the experimental references. In particular, the same decrease in $\gamma^N$, which has been associated to a ‘dirty’ (gas-exposed) metal surface, was confirmed by calculations. Thus, the applicability of the method to plastic material was considered to give realistic results. The computed $\gamma^N$ values associated to polyethylene are in the order of $10^{-1}$ for most of the ionic species here considered.

Moreover, we have observed that a few percentage points of variations of the surface energy levels predicted by DFT calculations, may cause, depending on the ion type, a substantial change of $\gamma^N$. Therefore a detailed sensitivity analysis has been included to address this problem. The results associated to metals have shown that $\gamma^N$ variations are, for some types of ions, very sharp, while this variability is milder for a polyethylene surface.

Our calculations are fully compatible with the previous relevant literature and suggest that plastic materials are characterized by $\gamma^N$ coefficients similar to those of metals only slightly smaller.

Keywords: secondary electron yield, polyethylene, first-principles calculations (DFT), Auger neutralization

(Some figures may appear in colour only in the online journal)
1. Introduction

This work reports the theoretical calculation of the secondary emission coefficient from a polyethylene surface through the Auger neutralization mechanism \( \gamma^N \) [1]. Moreover, we have investigated theoretically the secondary emission properties of metallic surfaces in order to support the reliability of the method applied to plastic materials. The \( \gamma^N \) coefficient has been estimated for the collision of 17 different types of cations on the two different types of walls considered.

Due to its low cost and suitable dielectric properties, polyethylene is a polymer employed especially in electrical power industry where it is used as an insulating material. Unfortunately, under thermal and electrical stresses it ages leading, in many cases, to an unpredictable failure of electrical components. In AC power supply systems the main aging phenomenon is the treeing [2, 3]; a series of small discharges takes place inside some cavities embedded in the polymeric bulk. The accumulation of damages caused by discharges lead to the formation of a cluster of channels (also known as treeing branches) through the polyethylene matrix. When these channels bridge the gap between the electrodes then the final failure of the insulating material occurs.

Each discharge is triggered by the release of a Schottky electron from the surface in a gaseous cavity, see [4]. If the electric field inside the void is strong enough, the electron will undergo an avalanche effect. The resulting discharge gives rise to the formation of ions, radicals and other reactive chemical species. These species attack the polymeric walls leading to a propagation of the treeing. The impact of ions with the walls of the cavity triggers the release of further electrons through the Auger effect thus sustaining the discharge activity. In spite of the large literature on this topic, the process of treeing evolution is still poorly understood and this leads to a great uncertainty when estimating the residual life of electrical components.

Simulation tools, based on the solution of a set of partial differential equations (PDEs), are now massively used to shed light on the treeing, the aging of polyethylene and, more in general, the aging of all polymeric insulating materials. Firstly, these kinds of tools have been applied to study the evolution of discharges in air such as corona and Trichel phenomena [5, 6]. The interaction of plasma with polymeric surfaces was included to address dielectric barrier discharges (DBDs), see [7, 8]. Then also the discharges in internal voids embedded in a polymeric matrix were included, see [9–11]. These latter simulations share many aspects of the physics of the propagation of discharges through treeing channels although the geometries considered are rather simplified: in many cases the voids have a spherical shape.

These simulation tools require knowledge of a large set of physical parameters some of which are rather poorly known. The quality of these kinds of simulations is to some extent strongly linked to the uncertainty of these parameters and, among them, the secondary emission coefficient plays a key role. Until now, this parameter has mainly been fitted to match the experimental data. In many cases, it is estimated that, for a metallic surface, its value varies in the interval 0.001–0.01, see [6, 12]. At least these values make it possible to match the period of some Trichel pulse experiments. Unfortunately, little is known about the useful values of \( \gamma^N \) to be used for polymeric surfaces and this has motivated the authors to undertake a first study on this aspect.

To be more specific, in plasma simulations, the total \( \gamma \) is what really matters, i.e. the result of the sum of all the possible secondary emission mechanisms. These processes can be split into those generated by a kinetic emission mechanism, and those triggered by a potential emission mechanism. It is already known [1, 13] that for slow ions (\(< 1\) keV) colliding on a metallic surface, the kinetic mechanism is negligible. On the other hand, it is also known that for the ionic dielectric system \( \text{MgO} \) [14–17] the kinetic emission becomes important for energies in the order of 10–100 eV. To the best of authors’ knowledge, there are still no references regarding the kinetic emission for plastic materials.

As regards the potential emission mechanism, electron ejection (Auger effect) might be triggered by ions (\( \gamma_i \)) or metastable species (\( \gamma_m \)). The treatment of excited states would require the use of a more expensive theory such as TD-DFT, and this is beyond the purposes of the present work. The ionic collision might cause an electron ejection through the Auger neutralization process (\( \gamma^N \)) or through the two-step Auger de-excitation mechanism (\( \gamma^D \)). In [1] it has been demonstrated that, for ions impinging on a metallic surface, \( \gamma^D \) is negligible compared to \( \gamma^N \). Moreover, in [18] is explained how the two-stage mechanism requires a relatively numerous series of energetic conditions. Therefore Auger de-excitation occurs much less frequently than Auger neutralization.

In the present work, we want to follow the same approach used in the computational study by Cho et al [14], where the authors have focused on the calculation of \( \gamma^N \). In the same work, they have dealt also with the kinetic emission mechanism from various \( \text{MgO} \) surfaces. On the contrary, the present work has focused only on the evaluation of \( \gamma^N \). However, we will show in section 3 that, in this particular case, the kinetic emission can be disregarded.

Our theoretical study of secondary electron emission has started considering a metal surface, and that’s because, for similar systems, this subject has a fairly rich literature to refer to [1, 13, 19, 20]. To the best of the authors’ knowledge, the secondary emission properties of insulating metal oxides such as \( \text{MgO} \) have been largely studied both with an experimental [15, 21, 22] and a theoretical/computational approach [14, 18, 23, 24]. However, this is not valid for all polymeric materials.

In this work, an investigation on pure and defective or oxidized metal surfaces have been carried out. These latter results have provided some preliminary tests in order to ensure the validity of our approach. We have evaluated \( \gamma^N \) associated to the surfaces of \( \text{Al} \) (001), \( \text{Cu} \) (001), \( \text{Cu}:\text{N} \), \( \text{Cu}:\text{O} \) and \( \text{CuO} \) (001). Aluminum and copper are two of the mostly used conductors in electrical devices, and this is one of the reasons why they have been considered. Our aim was to reproduce the trend and the order of magnitude reported in the review of experimental analysis in the work of Phelps et al [13].

In this work, we have evaluated SEY associated with the impact of the following ions: \( \text{N}^+ \), \( \text{N}_2^+ \), \( \text{N}_3^+ \), \( \text{N}_4^+ \), \( \text{O}^+ \), \( \text{O}_2^+ \).
In a gas ions drift due to the electric field and their approach speed depends upon their mobility and the actual electric field on the surface. We have considered a rather large interval ranging from $10^{-3}$ MV m$^{-1}$ to $10^2$ MV m$^{-1}$ which covers almost all the conceivable discharge conditions in electrical devices.

As outlined in [14], the estimation of $\gamma^N$ requires only the evaluation of a couple of convolution integrals whose characteristics depend upon some parameters that are derivable from first-principles calculations using DFT. Nevertheless, the original formulation of [27] plans to consider a series of corrections of the main parameters. As it will be explained in detail in the following section, these modifications have been neglected. The same choice was made in the work by Cho et al [14].

Our analysis has been complemented by a sensitivity analysis consisting in small variations of the fundamental surface energy parameters determining $\gamma^N$. This allowed us to provide data which take into account possible intrinsic inaccuracies embedded in an electronic structure DFT calculation. In particular, we have seen that even really small variations can affect the value of $\gamma^N$ to a large extent.

In the calculations associated to the metallic surfaces, our benchmark was mainly the ion Ar$^+$. This was done for reproducing, as close as possible, the experimental data of Cu-based species. We basically obtained a good agreement with the results reported by Phelps et al [13]. Indeed we found a $\gamma^N$ value in the order of $10^{-1}$ for clean metallic surfaces (Cu and Al) and an appreciable decrease (one order of magnitude) of $\gamma^N$ when we have considered an oxidized surface (CuO).

The experimental results reported by Phelps et al [13] distinguish between emission provoked by metastable species ($\gamma_m$) and that cause by ions ($\gamma_i$), but not between $\gamma^N$ and $\gamma^D$. However, the relative infrequency of two-stage events (see [1]) makes it possible to directly compare our results with those reported by Phelps [13].

Even though we found no experimental comparison of SEY for polyethylene, our result with the Ar$^+$ ion ($\gamma^N = 0.2204$) is, at least, comparable with Hagstrum’s theoretical analysis performed considering Ge (1 1 1) [27] (reproduced by computational modelling in [28]) and the numerical results of [14, 23] for pure and defective MgO.

The structure of the paper is the following. The next section is dedicated to the description of the integrals for the estimation of $\gamma^N$ and the computational setup for DFT simulations. Results are listed in section 3, while a critical review of the data obtained is included in section 4. Section 5 concludes the paper.

2. Methods

We have considered the polymer geometry shown in figure 2 which represents a realistic configuration of the interface between a polyethylene lamella and an amorphous phase or microscopic void [29, 30]. This system has adjacent polymeric chains connected by four methylenic units. This arrangement allows to maintain the continuity of chemical bonds, thus avoiding any formation of unsaturated centers or exposed methyl groups. Nevertheless, in the literature, several other arrangements have been considered. For instance, in [4] authors have performed DFT calculations on the (1 1 0) slab of polyethylene, reporting a band gap between 5.7 and 5.8 eV. The structure considered here presents a band gap equal to 5.83 eV, and the electronic structure is substantially unchanged between the various crystalline exposed faces.

As regards the ab initio modeling, we have used Quantum ESPRESSO, which is an integrated suite of computer codes for solid-state and electronic-structure calculations based on DFT, plane waves, and pseudopotentials [31]. We have performed calculations on slab systems of polyethylene, clean Al, Cu (both clean and with adsorbates) and pure CuO. We have extracted for each system the density of states (DOS) distribution $D(\varepsilon)$ and the Fermi energy $\varepsilon_F$ by first performing a self consistent field (scf) calculation, then a non–scf calculation with an increased sampling of the reciprocal cell. The subsequent plotting led us to identify the energy position of the VB top ($\varepsilon_v$), VB bottom (for the sake of convenience shifted to 0) and CB bottom ($\varepsilon_c$). Next, we have extracted the map of the electrostatic potential energy averaged in the plane perpendicular to the c-axis (i.e. along the thickness of each slab). Vacuum level $\varepsilon_0$ is obtained as the energy corresponding to the flat plateau of the electrostatic potential in the vacuum region.

This energetic description is needed to implement and solve the integrals which appear in the definition of $\gamma^N$ that we are going to introduce; see also [14, 18].

We point out that the resulting value of $\gamma^N$ strongly depends on the ionization potential of the incoming ion $E_i$ [1, 27, 32]. To be precise, this value is dependent on the fluctuations of the energy levels resulting from the approach of the ion towards the surface. This implies that the actual value of $\gamma^N$ depends on the distance $s$ of the ion from the surface. On the other hand, experimental observations demonstrated that the transition probability $P_i(s, v)$, where $v$ is the approaching speed, reaches a maximum at $s = s_m$ [1, 18, 27]. Therefore, to model a good approximation of $\gamma^N$, one should know the value of $s_m$, and from that calculate the related ionization potential $E_i^r$ to replace $E_i$. $E_i^r$ is defined as

$$E_i^r(s) = E_i + E(i - \text{surf}) - E(n - \text{surf}),$$

where $E(i - \text{surf})$ and $E(n - \text{surf})$ are the energies of interaction of the ion and the neutral species with the surface,
as described in [1, 27]. However, in practical calculations, it is really difficult to know the exact value of $s_m$ or even $E(i - surf)$ and $E(n - surf)$. For instance, Hagstrum obtained these quantities by fitting experimental data [27].

In the present work, we are mainly interested in reproducing at least the order of magnitude of experimental results of $\gamma^N$ in metals, and then in applying a very similar strategy to polyethylene. For this reason, as it will be shown in section 3, we have chosen to calculate the ionization potentials of the species in vacuum. These were taken from the literature, as done by [14], or obtained with DFT calculations in vacuum. In the latter case, we have simply performed two scf cycles of the molecule isolated, once neutral and once ionized. The ionization potential has been obtained as: $E_i = E^{\text{scf}}(\text{ion}) - E^{\text{scf}}(\text{neutral})$. The secondary emission coefficient can be computed as:

$$\gamma^N = \frac{\int_{E_{\text{max}}(\epsilon, \xi, \epsilon_c)}^{E_{\text{max}}(\epsilon_0, \epsilon_c)} P_\epsilon(\epsilon) D_i(\epsilon) \times \frac{\epsilon + \epsilon_0 - E_i}{2} d\epsilon}{\int_{E_{\text{max}}(\epsilon_0, \epsilon_c)}^{E_{\text{max}}(\epsilon_c, \epsilon_c)} D_i(\epsilon) \times \frac{\epsilon + \epsilon_0 - E_i}{2} d\epsilon} \times \delta(\epsilon - \epsilon_1 - \epsilon_2 + \epsilon_0 + E_i) d\epsilon d\epsilon_2$$

(2)

For a detailed discussion of the theory, the reader can also refer to [33]. For the sake of convenience, here we have labeled $\epsilon_b = E_i - \epsilon_0$, i.e., the depth (energy distance) of the hole energy level from the bottom of the band, which has been taken as the zero of the scale. $E_{\text{max}}$ represents the maximum kinetic energy with which an electron could be ejected [14, 18] (refer also to figure 1). $P_\epsilon$ is the ‘escape probability’ [27], defined as

$$P_\epsilon = \frac{1}{2} \left[ 1 - \left( \frac{\epsilon_0}{\epsilon} \right)^{\beta \gamma^N} \right] \alpha$$

(3)

This function defines the ejection probability dependent on the angle that the electron trajectory forms with the surface.

The two parameters $\alpha$ and $\beta$ are indeed adjustable coefficients that have been set equal to the reference values of $\alpha = 0.248$ and $\beta = 1.0$ according to some empirical observations associated to He$^+$ ions on a Ge surface; see [27]. Since these parameters are not well known for insulating materials, then we have also performed, in that case, a sensitivity analysis.

$T$ is the Auger transform [1, 27, 34], and it is defined as:

$$T \left[ \frac{\epsilon + \epsilon_0 - E_i}{2} \right] = \int_0^{E_0} \int_0^{E_i} D_i(\epsilon_1) D_i(\epsilon_2) \times \delta(\epsilon - \epsilon_1 - \epsilon_2 + \epsilon_0 + E_i) d\epsilon_1 d\epsilon_2$$

(4)

$D_i$ and $D_c$ are the DOS functions of the valence band and the conduction band, respectively. Once again, the rigorous application of the theory of Hagstrum would provide some corrections. $T$ would have to be subject to the convolution with a broadening function, obtainable from the fitting of experimental data. However, this effect becomes more important when an ion approaches the surface with high kinetic energy. Moreover, $D_i$ should be weighted with an appropriate function, which introduces a variation, depending on energy, of the transition probability through the valence band. This latter correction is necessary to have a discrimination against electrons $s$ and $p$ lying at the top of the band, which have different symmetry characteristics and different transition probabilities [27]. Also these corrections, according to Cho et al [14], have been neglected.

Definitions of $\gamma^N$ and $T$ are suitable for systems with energy gaps. Nevertheless, integrals can be adapted to be applied to a metallic system. This was done by simply replacing both $\epsilon_1$ and $\epsilon_c$ with $\epsilon_F$. Redefining the limits of integration in this way, the distribution $D(\epsilon)$, which for metals is continuous, is appropriately divided into populated and not populated portions.

2.1. PAW-DFT computational setup

Since the unit cells we have optimized were large, the derived reciprocal cells were small in volume. Therefore all the simulations were carried out by setting only one k-point in the I’ position of the Brillouin zone. Ultra-soft pseudo-potentials related to an Hamiltonian with PBE exchange-correlation functional, see [35], were employed throughout. For the polyethylene slab, the energy cut-off was set to 35 Ry, and the vacuum length of the optimized structure was 14.15 Å. For Al (001) the energy cut-off was set to 35 Ry with 17.5 Å of vacuum. For pure and defective Cu (001) slabs the cut-off was 40 Ry and the vacuum length 14.5 Å. In the case of the CuO (001) the cut-off was set to 35 Ry, with 20 Å of vacuum.

3. Results

In this section we present our results of the SEY calculation associated to the collision of several ions on both metallic and plastic surfaces. For many species, the ionization potentials have been derived from the literature. Nevertheless, for those species for which no references were found, i.e. N$^+$, O$^+$, O$_2^+$,
Table 1. $\gamma^N$ for a clean Al (0 0 1) surface for different types of ions. ● $E_i$ experimental and $^\circ E_i$ calculated.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$E_i$/eV</th>
<th>$\gamma^N$</th>
<th>$\gamma^N$ min</th>
<th>$\gamma^N$ avg</th>
<th>$\gamma^N$ max</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$^+$</td>
<td>14.54</td>
<td>0.2221</td>
<td>0.1120</td>
<td>0.2109</td>
<td>0.2671</td>
</tr>
<tr>
<td>N$_2^+$</td>
<td>15.58</td>
<td>0.2228</td>
<td>0.1121</td>
<td>0.2117</td>
<td>0.2691</td>
</tr>
<tr>
<td>O$^+$</td>
<td>10.98</td>
<td>0.2137</td>
<td>0.1116</td>
<td>0.2015</td>
<td>0.2467</td>
</tr>
<tr>
<td>N$^+$</td>
<td>7.83</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>O$^+$</td>
<td>13.60</td>
<td>0.2212</td>
<td>0.1120</td>
<td>0.2100</td>
<td>0.2650</td>
</tr>
<tr>
<td>O$_2^+$</td>
<td>12.07</td>
<td>0.2179</td>
<td>0.1120</td>
<td>0.2068</td>
<td>0.2590</td>
</tr>
<tr>
<td>NO$^+$</td>
<td>9.26</td>
<td>0.1579</td>
<td>0.0000</td>
<td>0.1301</td>
<td>0.2010</td>
</tr>
<tr>
<td>N$_2$O$^+$</td>
<td>12.89</td>
<td>0.2202</td>
<td>0.1118</td>
<td>0.2089</td>
<td>0.2629</td>
</tr>
<tr>
<td>NO$_2^+$</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>H$^+$</td>
<td>13.61</td>
<td>0.2212</td>
<td>0.1119</td>
<td>0.2100</td>
<td>0.2651</td>
</tr>
<tr>
<td>H$_2^+$</td>
<td>15.41</td>
<td>0.2226</td>
<td>0.1121</td>
<td>0.2116</td>
<td>0.2688</td>
</tr>
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<td>H$_3^+$</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.0681</td>
<td>0.1770</td>
</tr>
<tr>
<td>OH$^+$</td>
<td>13.75</td>
<td>0.2213</td>
<td>0.1120</td>
<td>0.2101</td>
<td>0.2654</td>
</tr>
<tr>
<td>H$_2$O$^+$</td>
<td>13.76</td>
<td>0.2214</td>
<td>0.1120</td>
<td>0.2101</td>
<td>0.2655</td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td>4.38</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>15.76</td>
<td>0.2229</td>
<td>0.1121</td>
<td>0.2119</td>
<td>0.2695</td>
</tr>
</tbody>
</table>

Table 2. $\gamma^N$ for a clean Cu (0 0 1) surface for different types of ions. ● $E_i$ experimental and $^\circ E_i$ calculated.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$E_i$/eV</th>
<th>$\gamma^N$</th>
<th>$\gamma^N$ min</th>
<th>$\gamma^N$ avg</th>
<th>$\gamma^N$ max</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$^+$</td>
<td>14.54</td>
<td>0.1743</td>
<td>0.0000</td>
<td>0.1292</td>
<td>0.2101</td>
</tr>
<tr>
<td>N$_2^+$</td>
<td>15.58</td>
<td>0.1810</td>
<td>0.1448</td>
<td>0.1880</td>
<td>0.2379</td>
</tr>
<tr>
<td>O$^+$</td>
<td>10.98</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>N$^+$</td>
<td>7.83</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>O$^+$</td>
<td>13.60</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0667</td>
<td>0.1737</td>
</tr>
<tr>
<td>O$_2^+$</td>
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<td>0.0000</td>
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<td>0.0000</td>
</tr>
<tr>
<td>NO$^+$</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>NO$_2^+$</td>
<td>9.26</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>N$_2$O$^+$</td>
<td>12.89</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0248</td>
<td>0.1374</td>
</tr>
<tr>
<td>NO$_2^+$</td>
<td>6.88</td>
<td>0.0000</td>
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<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>H$^+$</td>
<td>13.61</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0672</td>
<td>0.1742</td>
</tr>
<tr>
<td>H$_2^+$</td>
<td>15.41</td>
<td>0.1767</td>
<td>0.1353</td>
<td>0.1832</td>
<td>0.2333</td>
</tr>
<tr>
<td>H$_3^+$</td>
<td>8.68</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>OH$^+$</td>
<td>13.75</td>
<td>0.0818</td>
<td>0.0000</td>
<td>0.0745</td>
<td>0.1805</td>
</tr>
<tr>
<td>H$_2$O$^+$</td>
<td>13.76</td>
<td>0.0896</td>
<td>0.0000</td>
<td>0.0752</td>
<td>0.1815</td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td>4.38</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>15.76</td>
<td>0.1856</td>
<td>0.1549</td>
<td>0.1928</td>
<td>0.2427</td>
</tr>
</tbody>
</table>

$H^+_i$, $OH^+_i$, $H_2O^+$, this energy parameter was obtained through DFT calculations.

Since the energy parameters which, in the definition, determine the integration range in $\gamma^N$ (such as $\xi^i$) were obtained through DFT calculations, their numerical value may be affected by a certain degree of uncertainty. Moreover, since we have neglected the corrections mentioned in section 2, we have evaluated the integrals in (2) and (4) considering a variation of ±10% for the following parameters: $\xi, \epsilon_0, \epsilon_r, \epsilon_f$. The variations have been evenly spaced in a ±10% range, centered in our reference value$^6$. The interval has been sampled by executing the code a statistically significant number of times, which in our case turned out to be 30. We have seen that a finer spacing does not lead to a strong variation of the results.

The results obtained from calculations on metallic surfaces are presented in section 3.1 (tables 1–4) while the results for polyethylene slab are reported in section 3.2 (tables 4–6).

3.1. Metallic surfaces

We have considered Al (0 0 1) as the first metallic surface system, the DOS is plotted in figure 3$^7$. Table 1 shows the $\gamma^N$ values associated with the ion database together with Ar$^+$, which has been considered the most significant benchmark to evaluate the performance of the model.

In order to reproduce as closely as possible the situation described in the experimental works [13], a second performance test has been performed on clean and ‘dirty’

$^5$The work function is defined as $\xi = \epsilon_0 - \epsilon_f$, and both these two levels have been obtained through DFT calculation.

$^6$That is, the $\gamma^N$ value obtained in the first instance by using the energetic description produced by our calculation.

$^7$In this graph, and in all the DOS graphs reported in this paper, 0 have been set at the beginning of the energetic scale, that is the VB bottom.

(gas-exposed) Cu surfaces. Results of clean Cu are reported in figure 4 and table 2.

Moreover, the work by Phelps et al reports some outcomes associated with metallic surfaces exposed to gases like O$_2$ and N$_2$ which reported an appreciable decrease in SEY [13]. In order to check the model’s ability to reproduce this behavior, we have performed the same calculation on a Cu system with a single oxygen or nitrogen atom adsorbed on the metal surface. Anyway, no significant difference in $\gamma^N$ values has been observed. Therefore, we have decided to consider a more advanced oxidation degree, and a pure CuO system has
been included in our calculations. The results are reported in figure 5 and table 3.

In this case the drop of the $\gamma^N$ value is significant: the reference state is associated to a vanishing SEY while some small variations produce some non-zero $\gamma^N$.

3.2. Polyethylene surface

We have considered the conformation of the polymer described by Righi et al [30], which is represented in figure 2. In figure 6 we report the DOS diagram for both the bulk and the slab system of the polymer. From this graph it is possible to notice how the presence of surface states favors the narrowing of the energy gap. The states of the slab system around 15 eV are associated to the vacuum-exposed methylene groups, which link the polyethylene chains. The feature at around 20 eV is a diffused conduction state which springs from the formation of the surface/vacuum interface [36]. The results for $\gamma^N$ on polyethylene are reported in tables 4–6.

In the first instance, we point out how a plastic material behaves similarly to metals. In fact, we have obtained values of $\gamma^N$ in the order of $10^{-1}$ for most of the species considered. This was, to some extent, unexpected, due to the great difference, in terms of electronic transport, that exists between a metal and a plastic insulating material. Moreover, the sensitivity analysis with respect to the variations of the $\alpha$ (table 5) and $\beta$ (table 12) parameters proves that slight variations of these coefficients do not imply any major variation of $\gamma^N$.

Unlike what Cho et al did [14], as has already been pointed out in section 1, the treatment of the electron emission derived from a kinetic mechanism has not been included in this work. Nevertheless, we have adopted a similar strategy to assess the emission probability through kinetic mechanism. That is, we have performed a first-principles molecular dynamics (FPMD) simulation, reproducing what we can consider as one of the most extreme (but also frequent) plasma conditions we are interested in (i.e. $O_2^+$ with an impact energy of $\sim10eV$).8 At the beginning of the simulation the Fermi energy was 5.6 eV below the vacuum level, and during the dynamics (after the collision) it reached a maximum at 1.9 eV below the vacuum level. Unlike what was obtained by Cho et al, the Fermi energy of the entire system remains firmly below the vacuum level. Therefore, considering this result and the lack of any experimental reference which contradicts our findings, electron emission through kinetic mechanism can be disregarded.

4. Discussion

Regarding metal surfaces, we first consider the results of Al which is a relatively light metal, easy to computationally manage and often employed as a component in several electric devices such as high voltage power cables [37] and overhead lines [38]. Table 1 lists its SEY results corresponding to our complete ion database. Depending on the ionization energy, several different configurations may occur. If the potential energy of the ion is very low, then, even considering some variations of the surface energetic characteristics, the SEY vanishes. This is the case of $N_2^+$, $NO_2^+$ and $H_3O^+$. Then we have some boundary cases, such as the ones of $O_4^+$, $NO^+$, $H_4^+$, where the ionization is still too low to generate any secondary emission. However if we consider some variations of the energy levels produced by DFT electronic calculations,

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8The estimated energy of $\sim10eV$ corresponds to the expected kinetic energy of an $O_2^+$ ion drifted by an electric field of 30 MV m$^{-1}$, which is associated to the dielectric strength of polyethylene.
then we get some not-vanishing results in the upper end of the interval. The complementary case is the one for $N_2^+$, $O^+$, $O_2^+$, $N_2O^+$, $H^+$, $OH^+$ and $H_2O^+$ where the reference energy configuration leads to a not null $\gamma^N$ but, if we consider the lower spectrum of the variations, we can still get some vanishing values. Finally, the ions characterized by large ionization potentials, such as $N^+$, $N_2^+$, $H_2^+$ and $Ar^+$, have, in all cases, not null SEY values.

We also point out that, in many cases, the SEY value is either zero or close to $10^{-1}$. In other words, there are few intermediate values. This is due to the fact that $\gamma^N$ is very dependent on the specific value of the Auger transformation (4). This is, in fact, a convolution integral:

$$T \left[ \frac{\epsilon + \epsilon_0 - E_i}{2} \right] = \int_0^{\epsilon_i} D_i(\epsilon) D_A(\epsilon + \epsilon_0 + E_i - \epsilon_1) d\epsilon_1,$$  

between two shifted functions. To be more precise the function (i.e. $D_\epsilon$) is the same. If the shift $\epsilon + \epsilon_0 + E_i$ is small, then there is no overlap between the original and the shifted function which leads to a vanishing result. On the contrary, if the shift is large enough, then the two functions have a non-null overlap and $T \left[ \frac{\epsilon + \epsilon_0 - E_i}{2} \right] \neq 0$. In these cases $\gamma^N$ is mainly controlled by $P_\epsilon$ and the specific shape of the DOS of Al (see figure 3). This induces $\gamma^N$ to rapidly saturate at values of $10^{-1}$, as confirmed by [22].

Table 2 lists $\gamma^N$ associated to an ideal Cu surface. In this case, only a few ions report an ejection probability different from zero. For ions that produce some non-vanishing emission results, such as $H^+$, $O^+$ and $N_2O^+$ the $\gamma^N_{\text{max}}$ are close to $10^{-1}$, which is comparable with the results already shown for Al. Once again, we have evidence of how the $\gamma^N$ is very sensitive to the displacement, even minimal (at most $\pm 10\%$), of the energy levels of the surface system. From another point of view, these results are very different from the ones we got in the case of Al, where inert ions were only a minority. However, this can be explained by referring to the DOS function (see figures 3 and 4). The Cu system presents a state density plot typical of a transition metal, i.e. it has a strong band associated to $d$-electrons below the Fermi level and, at higher energies, a substantial flattening of the state density trend. On the other hand, the shape of the Al DOS presents a general trend that can be associated with the free electron gas distribution of energy $D(\epsilon) = C\epsilon^{1/2}$ [39].

The simulation of a ‘dirty’ Cu slab has been considered in order to compare its trends with the experimental data reported in the work of Phelps et al., where some metal surfaces exposed to various gases, such as $N_2$ and $O_2$, have been considered. This treatment seems to affect the final SEY, in particular $\gamma^N$ decreases by nearly one order of magnitude [13]. In order to reproduce this result in our computational work, a first attempt has been carried out with a Cu slab in presence of two kinds of adsorbates (O and N, respectively). The results, omitted here, do not lead to any substantial difference from the data produced by clean Cu system.

Therefore, we have considered the simulation of a system characterized by a marked increase of the oxygenation degree, i.e. a slab of Cu (II) oxide. The idea was to reproduce the
surface layer of oxide present in a real Cu system exposed to a normal atmosphere. The DOS plot of CuO is reported in figure 5, and the $\gamma^N$ results are collected in table 3.

Comparing it with table 2, a drastic reduction in the secondary emission values associated with the impact of each ion has been observed. To be more precise, the reference values of $\gamma^N$ (third column) vanish for all the types of ions. Although this is consistent with the trend we expected, these results probably underestimate the actual value of SEY. As a matter of fact, the sensitivity analysis highlights that variations of a few percentage points in energy levels are sufficient to obtain a significant secondary emission. In other words, a slightly variation of the shape of the escaping Auger neutralization process, associated to both metals and plastic materials, has been treated with a computational approach. Preliminary calculations on clean, defective and oxidized metal surfaces have actually reproduced experimental observations. In particular, the same decrease in $\gamma^N$ associated with gas-exposed surfaces reported by Phelps et al.

<table>
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<th>Ion</th>
<th>$E_i$/eV</th>
<th>$\gamma^N$</th>
<th>$\gamma^N_{\text{min}}$</th>
<th>$\gamma^N_{\text{avg}}$</th>
<th>$\gamma^N_{\text{max}}$</th>
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<tbody>
<tr>
<td>N$^+$</td>
<td>14.54</td>
<td>0.1861</td>
<td>0.1720</td>
<td>0.1863</td>
<td>0.2015</td>
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<td>N$^+_2$</td>
<td>15.58</td>
<td>0.2157</td>
<td>0.2006</td>
<td>0.2159</td>
<td>0.2320</td>
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<tr>
<td>N$^+_3$</td>
<td>10.98</td>
<td>0.0532</td>
<td>0.0477</td>
<td>0.0533</td>
<td>0.0594</td>
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<td>N$^+_4$</td>
<td>7.83</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>O$^+$</td>
<td>13.60</td>
<td>0.1575</td>
<td>0.1447</td>
<td>0.1577</td>
<td>0.1714</td>
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<tr>
<td>O$^+_2$</td>
<td>12.07</td>
<td>0.1026</td>
<td>0.0934</td>
<td>0.128</td>
<td>0.1128</td>
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<td>O$^+_3$</td>
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<td>NO$^+$</td>
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<td>0.0000</td>
<td>0.0000</td>
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<td>NO$^+_2$</td>
<td>12.89</td>
<td>0.1337</td>
<td>0.1223</td>
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<td>NO$^+_3$</td>
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<tr>
<td>H$^+$</td>
<td>13.61</td>
<td>0.1578</td>
<td>0.1450</td>
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<td>H$^+_2$</td>
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<td>0.2112</td>
<td>0.1962</td>
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<td>0.2274</td>
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<tr>
<td>H$^+_3$</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
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<tr>
<td>OH$^+$</td>
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<td>0.1619</td>
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<tr>
<td>H$_2$O$^+$</td>
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<td>0.1625</td>
<td>0.1495</td>
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<td>0.1768</td>
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<td>Ar$^+$</td>
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<td>0.2204</td>
<td>0.2052</td>
<td>0.2206</td>
<td>0.2368</td>
</tr>
</tbody>
</table>

5. Conclusions

Auger neutralization process, associated to both metals and plastic materials, has been treated with a computational approach. Preliminary calculations on clean, defective and oxidized metal surfaces have actually reproduced experimental observations. In particular, the same decrease in $\gamma^N$ associated with gas-exposed surfaces reported by Phelps et al.
[13] was confirmed by our calculations. Therefore, the applicability of the method to materials with different nature can be considered reliable.

Compared to the results obtained for metals, a similar strategy applied to plastic materials has originated slightly lower $\gamma^N$ values, even though with a comparable order of magnitude. If we consider that the electronic transport in a plastic is noticeably different compared to that in a metallic system, these data are, to some extent, unexpected. Anyway, our results are consistent with other computational works on insulating materials [14, 23].

The sensitivity analysis on $\gamma^N$, especially for metals, reported some high values ($\sim 10^{-1}$) in all cases where the impacting ions have a large ionization potential. On the other hand, if $E_i$ is not large enough SEY vanishes. Hence, in all other cases, $\gamma^N$ strongly depends on both surface conditions and the accuracy of the description of the electronic levels involved, i.e. the DFT calculation. It is worth noting that even experimental data are quite scattered in a $10^{-1} - 10^{-2}$ range [13]. Anyway, polyethylene data reported a smaller sensitivity to energy levels variation: in some cases the $\gamma^N$ magnitude is $10^{-2}$.

To the best of author’s knowledge, this is one of the first works devoted to Auger emission from plastic materials commonly used in electrical insulating systems. For some ions, our outcomes showed that SEY coefficients are much higher than the 0.001–0.01 range of values, which is currently used in the simulations of partial discharges in a gas [6, 12]. Therefore, a particular care must be taken as small variations of the composition of a given gas (for instance the humidity of air) may lead to a different composition of ions impacting surfaces and thus a different total secondary emission yield.

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