Effect of Chemical Impurities on Space Charge Density at the Interface between Polyethylene and Copper

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ABSTRACT The estimation of charge density distribution in polyethylene (PE) especially at the interface region with conducting material such as copper (Cu) is essential at high field conduction. The magnitudes of space charge at that interface depend on the applied electric field and the electrode material. In this work, the charge density is computed for a slab model of Cu (111)/PE (001) in its pure condition and then with chemical impurities present in the PE chains. The density-functional theory (DFT) is used as a computational quantum mechanics to evaluate the charge density in the interface region. An electric field is applied between vacuum regions attached to the model to study the effect of presence of chemical impurities on the distribution of charge density along the interface. The chemical impurities used in this study are carbonyl, vinyl and conjugated double bond. It is found that the peak value of negative charge density near the Cu atoms at the interface region decreases as the impurity-created barrier height decreases. It is also found that changes in the charge density near the interface region occur only within 6 Å inside PE chains; the charge density becomes constant thereafter, i.e., in the PE bulk. This paper reveals that the position of chemical impurities in PE chain influences the maximum change in charge density relative to its bulk values. The maximum change in charge density is found to be related to the trap depth in PE band gap, which is created by the presence of chemical impurities. It is concluded that the charge density distribution is affected by chemical impurities in PE and, in turn, affects the charge accumulation process.

INDEX TERMS charge density, chemical impurities, polyethylene, copper, barrier height, trap depth and density-functional theory (DFT).

I. INTRODUCTION

High field conduction enhances the space charge accumulation in dielectric material, e.g., Polyethylene, which may lead to aging [1], [2]. Those charges cause distortion in the electric field inside the dielectric and, hence, accelerate insulation degradation [4], [5]. Meanwhile, the interface region between different materials is of great interest as it can influence the whole characteristics of the materials [3], and this is where most of insulation failures start. Of special interest is the interface region between polyethylene and the electrode material, where charge transfer is noted. The presence of shallow and deep energy traps in the polyethylene band gap is strongly related to the amount of space charges accumulation [6-8]. These traps are formed due to the morphological effect of the interface with the electrode, or they are attributed to the presence of impurities in polyethylene [9], [10]. Chemical impurities in polyethylene process -such as carbonyl, vinyl and conjugated double bond- are formed during the manufacturing process [10]. These impurities cause a reduction in the barrier height between electrode Fermi level and the traps, which in turn facilitates charge injection. Many research works were carried out using different types of dielectric materials to measure -or develop models for- the charge injection process [4], [5], [13]. Pulsed electro-acoustic (PEA) method was used to measure the space charge in dielectric materials experimentally [11],[12]. This test was applied to a specimen of polymer material between two electrodes under an applied voltage, and the charge density characteristics were subsequently measured. Previous experimental studies were carried out using (PEA) to measure the space charge characteristics at different operating conditions. One of those studies used PE specimen to calculate space charge distribution at different temperature and voltage [1]. Also, different polymer materials were used in these experimental studies such as polyethylene, XLPE and Low-density polyethylene (LDPE) and High-density polyethylene (HDPE) [11-13]. The effect of
electrode type and temperatures on space charge distribution was shown in [14], [16]. Different forms of voltage were used to study the space charge, such as, AC [4], DC [5], or square pulse voltage [17]. A relation between space charge and trap energy over a range of temperature for XLPE specimen was developed experimentally [18]. A study on polyethylene-graft-poly(styrene/LDPE) composites were made, where DFT was subsequently used to calculate the trap energy [19]. Meanwhile, theoretical models of high field conduction were developed to interpret the experimental results based on Schottky injection, and the Fowler-Nordheim mechanism [3]. Schottky injection applies to electric fields below 100 kV/mm while Fowler-Nordheim is used for higher fields [14], [15]. Both models can be used in electrode-limited conduction, which is selected in the interface problems [3]. The interface model between polyethylene and copper was developed using computational quantum mechanics, which is based on density functional theory [9], [10]. An interface model was developed for Cu (111) and Au (111) with LDPE to simulate the charge density distribution using DFT and compared by Kelvin Probe Force Microscopy measurements (KPFM) [20].

The present work simulates the charge density distribution in the interface direction between Cu (111) and PE (001) under an applied external electric field. The cases of adding chemical impurities to the polyethylene is studied -using the interface model- and then compared to the pure material case. The comparison is carried out with regards to the charge density distribution in each case, where the postprocessing analysis is carried out to compute the charge density along the interface direction. This work focuses on the change in charge density at the interface region in the presence of chemical impurities. This change is correlated to the trap depth and barrier height under these circumstances. It is noted that, so far, no studies were made to compute space charges in polyethylene with chemical impurities using DFT, which this work aims to do.

II. METHODOLOGY AND MODELS

A. DENSITY FUNCTIONAL THEORY (DFT)

The density functional theory (DFT) is the computational quantum mechanics method that is used to solve high field conduction problems, such as that treated in this study. The DFT method was applied in similar previous studies by solving Schrödinger equations, while controlling the computational time and output parameters accuracy [21]. The Quantum Espresso code is developed to implement the DFT approximations [22]. These approximations include the Perdew-Burke-Ernzerhof (PBE) function within the generalized gradient approximation (GGA) that represent the exchange correlation potential. Troullier-Martins pseudopotentials are utilized for all atoms in all models. Also plane waves basis sets represent the wavefunction. More details about the energy conversion and computational data are found in [9], [10].

The interface model between polyethylene and Copper is prepared using the DFT approximations. The heterostructure of the interface model in X-Y plane consists of 2-unit cells of slab PE (001) and 6-unit cells of slab Cu (111). The number of unit cells in each slab model is selected to ensure the reduction of the lattice mismatch error on the interface X-Y plane. The slabs are extended in the Z direction to eliminate the image effect and to reproduce the bulk properties. Figures 1(a) and (b) show the standalone slabs of Cu and PE, respectively. Figure 1(c) shows the interface between the two materials. Each slab consists of a 6-unit cells layer with length about 27 Å; a vacuum layer is then added on each side of slabs. The vacuum length is about 10 Å to ensure the elimination of the image effect of polyethylene and copper atoms. The total heterostructure length in the Z direction along the interface direction is about 50 Å. The models are subjected to an external electric field of 100 kV/mm between the two vacuum surfaces in z direction, and the space charge density distribution in each case was sought. The planar average charge density (ρ) is computed as post processing analysis in quantum espresso code for each model. The differences between the computed charge density in PE/Cu interface model and that in the standalone Cu slab and the standalone PE slab are then deduced. This method was described in detail in [20]. The difference charge density Δρ is calculated as [20]:

$$Δρ = ρ_{Cu (111)/PE (001)} - ρ_{Cu (111)} - ρ_{PE (001)}.$$ 

Where $ρ_{Cu (111)/PE (001)}$, $ρ_{Cu (111)}$ and $ρ_{PE (001)}$ is the volume charge density (C/m$^3$) of the interface model, the slab copper model, and the slab polyethylene model respectively. The charge density distributions for all models are computed as a planar average value along the interface direction (Z direction).
A chemical impurity is then added individually at the outer chain of PE in the interface with Cu atoms in X-Y plane. The heterostructure of each model of chemical impurities was described in [10]. The above models are applied here with and without impurities to study the changes in the charge density under an applied external electric field. The charge density is computed along the interface of the pure Cu (111)/PE (001) model using the post processing analysis in quantum espresso code. This is repeated for each impurity. A comparison among different impurity models and pure case is held to examine the effect of chemical impurities on computed charge density, especially at the interface region.

III. RESULTS

A. Computed Charge density at the interface

When subjected to the external electric field, Figures 2 and Figures 3 show the distribution of charge density in standalone Cu, standalone PE, respectively. Figure 4 shows the distribution of charge density at the interface of the two materials. When the electric field is applied to the model, charges are transferred from the copper electrode to the dielectric (polyethylene). As expected, the charge density in the vacuum regions is zero. The charge density in bulk polyethylene is found to be about $43.5 \times 10^6 \text{ C/m}^3$, whereas in copper it fluctuates around $155 \times 10^6 \text{ C/m}^3$. 

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**Figure 1.** Different configurations of PE (001) and Cu (111) with the external field.

**Figure 2.** Computed charge density for slab Cu (111).

**Figure 3.** Computed charge density for slab PE (001).

**Figure 4.** Computed charge density for a pure case of Cu/PE interface model.
B. Influence of PE-Cu interface on space charge

The changes undergone by the charge density due to the interface between Cu and PE is deduced. The changes in charge density, which are materialized due to joining the two materials are depicted in Figure 5. Over the atomic zone of each material seen previously in Figure 1- those changes are based on the results of Figures 2, 3 and 4.

It is to be noted that the change in space charge density due to the interface of PE and Cu is confined to the zone between 11 to 15 Å as shown in figure 5. The peak negative charges seen in the figure near the Cu slab at the interface region indicate a positive injection from the electrode to the dielectric. The magnitude of the injection depends on such factors as the polarity and material of electrode [14]. Also, the work function of the electrode material influences the charge injection and the values of space charge at the interface [23]. Similarities are seen between the computed distribution of charge density at the interface and that deduced in an experimental study [23]. That study used a low-density polyethylene (LDPE) specimen of about 0.5 mm with aluminum plates and used a pulsed electro-acoustic (PEA) method to measure the charge density distribution under different fields [23].

The surface charge density \( \sigma_s \) is calculated on the basis of

\[
\sigma_s = \int_0^L \Delta \rho \, dz.
\]

where, \( dz \) is in the direction along the interface; \( \rho \) is the volumetric charge density. The calculated value of \( \sigma_s \) in the interface model Cu (111)/PE (001) is 0.02067 C/m².

Since the barrier height is known to change due to the presence of chemical impurities in polyethylene [10], the following sections will find out the effect of those impurities on charge densities.

C. Impact of carbonyl impurities on space charge density

Two different models for carbonyl and terminal carbonyl were developed in a previous study [10] using DFT approximations in Quantum espresso code. For each model, the charge density is computed in this work as a post processing analysis. The space charge distributions for the interface model Cu (111) and PE (001) in the presence of carbonyl and terminal carbonyl impurities are computed and are shown in Figure 6.

In Figure 6, the peak negative charge noted at the interface near Cu face in carbonyl impurity Cu/PE model is \(-38.261 \times 10^6 \text{ C/m}^3\), while with terminal carbonyl impurity Cu/PE model it is \(-36.133 \times 10^6 \text{ C/m}^3\).

D. Impact of vinyl and conjugated double bond impurities on space charge density

Models for vinyl and conjugated double bond were developed in a previous study using DFT approximations in Quantum espresso code [10]. The charge density is computed in this work as a postprocessing analysis for each model. The space charge distribution for the interface model Cu (111) and PE (001) in the presence of vinyl and conjugated double bond impurities are depicted in Figure 7.
In Figure 7, the peak negative charge noted at the interface near Cu face in vinyl impurity Cu/PE model is $-44.075 \times 10^6$ $C/m^3$, while with conjugated double bond impurity Cu/PE model it is $-34.161 \times 10^6$ $C/m^3$.

Figure 8 offers a comparison among the changes undergone by space charge density in the case of pure material and those in the presence of chemical impurities. The space charge distributions for all impurity models are compared with the pure case of Cu/PE as shown in Figure 8. It is found that the position of chemical impurity in PE chain at the interface produces a change in charge density. This change begins at distance 12 Å to 15 Å as shown in Figure 9. The maximum charge density is noticed at the chemical impurity position at 13.1 Å along the interface.

### E. Space Charge and Barrier height

This work examines the relation between the barrier height in dielectric material and the peak negative charge density near Cu atoms at the interface with PE chains. The barrier height is the difference between the Fermi level and the trap depth in band gap of PE. In the case of pure materials (Figure 5), the peak negative charge seen at the interface near the Cu face –in the pure material case of Cu/PE– is $-45.9188 \times 10^6$ $C/m^3$, while–based on a previous work [9]– the calculated holes injection barrier was 3.54 eV.

Table 1 shows the values of peak negative charge density and the calculated barrier heights for the pure material case and with chemical impurities present. It is found that a higher peak negative charge density is associated with higher barrier heights. This means that under the same external field- charge injection is enhanced due to the presence of chemical impurities especially those that have deep traps.

### Table 1. The peak negative charge density and the calculated barrier heights for different models.

| Chemical impurity          | Peak negative charge density ($10^6$ $C/m^3$) | Barrier height (eV) [9], [10] |
|----------------------------|-----------------------------------------------|-----------------------------|
| Pure case                  | $-45.9188$                                     | 3.54                        |
| No impurity                | $-38.261$                                      | 2.79                        |
| Carbonyl                   | $-44.075$                                      | 3.25                        |
| Vinyl                      | $-34.161$                                      | 2.49                        |

The charge density in bulk PE after the change between 15 to 25 Å is about $-1.3 \times 10^6$ $C/m^3$ for all models (with and without chemical impurities). The next section studies the difference between the bulk value of charge density and the maximum charge density at the impurity location as seen in Figure 9.

### F. Space Charge and Trap Depth

The difference between the bulk value of charge density and the maximum charge density at the impurity location is calculated. These values are linked to the trap depth in PE due to the presence of chemical impurities. The trap depth is the depth of an occupied impurity state above the valance band maximum (VBM). It was calculated in a previous study [10] for the types of chemical impurities used in this work. The magnitude of maximum change of charge density and the corresponding trap depth of chemical impurities are given in Table 2. It is found that the maximum change of charge density systematically decreases at higher trap depths. This implies that charge injection is easier with deeper trap depth, such as in the case of conjugated double bond.

### Table 2. The higher charge density at impurities position and the calculated trap depth for different impurity models.

| Chemical impurity          | Maximum change of charge density ($10^6$ $C/m^3$) | Trap depths (eV) [10] |
|----------------------------|-------------------------------------------------|-----------------------|
| Carbonyl                   | 0.742                                           | 1.31                  |
| Terminal Carbonyl          | 4.753                                           | 0.62                  |
| Vinyl                      | 3.386                                           | 0.85                  |
| Conjugated double bond     | 0.273                                           | 1.61                  |
Conclusions

The DFT model of Cu (111)/ PE (001) both in its pure condition and in the presence of chemical impurities is used to determine the space charge distributions under an applied electric field of 100 kV/mm. In the pure case, the charge density varies with distance about 6 Å in PE chains at the interface due to the high field conduction from Cu to PE. A peak negative charge density is noticed at the interface for a pure case model is about $-45.9188 \times 10^6$ C/m$^2$.

Compared to the stand-alone materials, a significant change in charge density appears at the interface region between the Cu electrode and PE. The change in charge density in PE chains occurs over the first two-unit cells from the interface with Cu, i.e., over a distance of about 6 Å. Meanwhile, the charge density within the bulk PE beyond the change between 15 to 25 Å is about $-1.3 \times 10^6$ C/m$^2$. The distribution pattern of the charge density at the interface matches that reported in an experimental study [23]. It is concluded that the charge density at the interface between PE/Cu is significantly affected by the presence of chemical impurities. The magnitude of the peak negative charge density at the interface is related to the calculated injection barrier height for each case. It is found that a chemical impurity with a lower injection barrier height, such as the conjugated double bond, has a smaller peak negative charge density of $-34.161 \times 10^6$ C/m$^3$, which indicates higher charge injection than that in the case of pure material model. It is also found that the maximum change of charge density at the location of chemical impurity in the PE chain and the bulk PE value is related to the trap depth of impurities from the VBM.

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