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# Dependence of the Field and Charge Distribution at a Semicon/Polyethylene Interface on the Press-Molding Process Derived from Kelvin Probe Force Microscopy

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**Abstract-** Knowledge about the electronic properties of interfaces between different materials is fundamental for understanding charge transfer. This is particularly relevant in High Voltage Direct Current (HVDC) polyethylene (PE) insulated power cables with semicon (SC) electrodes. We investigate the PE-SC contact interface of lab made SC/PE/SC slices using Peak Force - Quantitative Nano Mechanics (PF-QNM) and Kelvin Probe Force Microscopy (KPFM) techniques. Field and charge distributions are derived at nanoscale and compared for different PE cover-layer materials (PolyEthylene Terephthalate (PET) or Aluminum (Al)) used during the molding process. Whatever the process, negative or positive charge clouds spread over 2-3  $\mu\text{m}$  in PE. The maximum charge density is strongly influenced by the cover-layer material, in correlation with the diffusion of oxidized groups from PET, in spite of a smoother roughness when compared to Al. We also report on results where a small voltage was applied to the structure.

## I. INTRODUCTION

Electronic properties of interfaces between conducting/semi-conducting electrodes and a dielectric layer can strongly influence charge transfer [1, 2, 3]. The theoretical contact potential barrier (metal work function minus dielectric electron affinity) cannot explain the measurements [4], and it has been proposed that the interfacial electronic properties control the charge transfer. Recent approaches focus on ab initio modeling in order to unravel the nature of these states in model situations [5, 6]. The discrepancy between theoretical potential barriers and those obtained through charge transport modeling with fluid models [7] is another evidence that the description of interfacial properties is not satisfactory. In spite of this, very few studies aimed at investigating experimentally the interfacial electronic properties in situations of interest for electrical engineering design. Owing to the increasing development of HVDC technologies, especially polyethylene insulated power cables for energy transport, we focus on carbon black (CB) filled host polymer (SC) / PE interfaces.

We recently reported on chemical, structural and dielectric nanoscale properties of such interfaces [8, 9]. The bare PE was studied by Photoluminescence (PL), Infrared Spectroscopy (IR) and Atomic Force Microscopy (AFM) to characterize the morphology and the chemical properties of the films. Macroscopic electrical properties were also investigated by charging/discharging current and space charge measurements.

It appears that when using polyethylene terephthalate (PET) as protective cover layer during press-molding process, extra signatures appear in PL and IR spectra related to diffusion of oxidized groups – presumably decomposition products from PET into the PE surface. Also changes in surface roughness appear, depending on the nature of the cover layer, PET or Al. However, the different press-molding conditions did not reveal substantial changes in the formation of space charge, and the nature of electrode remains the most influencing factor for space charge and conduction features. In this work we show that press-molding conditions have an impact on the charges near the SC-PE contact.

## II. EXPERIMENTAL

### A. Peak Force - Quantitative Nano Mechanics and Kelvin Probe Force Microscopy

The interfacial properties at SC/PE interfaces were investigated by Peak Force Amplitude Modulation Kelvin Probe Force Microscopy (PF-AM-KPFM) using the AFM Multimode 8 from Bruker which combines two different AFM modes: Peak-Force Quantitative NanoMechanical (PF-QNM) which probes the topography and mechanical properties (adhesion, deformation, Young modulus) [10] and Kelvin Probe Force Microscopy (KPFM) which probes the surface potential [11]. A PtIr coated Si tip and a lift of 40 nm were used.

### B. Sample preparation

The sample preparation procedure is described in [8]. We used a nonstabilized low-density polyethylene from ExxonMobil™ (LDPE LD 101BA). The SC was produced by mixing acetylene black nanoparticles to the PE compressed into granules. These materials are used to realize a three layered sandwich-like structure SC-PE-SC with a thickness of 150  $\mu\text{m}$ . Each layer is 50  $\mu\text{m}$  thick and produced in a hot-press by heating at 140°C. To avoid the films sticking to the metallic surface of the mold, we introduced a cover layer of PET or Al. The three layers are subsequently heated together to 110°C under a small pressure to ensure an intimate contact. Then, cross sections of 200 nm in thickness are taken from the sandwich structure using ultra-cryo-microtomy. The semicon is grounded during KFM measurements.

### III. RESULTS AND DISCUSSION

#### A. PFQNM and KPFM profiles

Fig. 1 gives surface potential profiles for the sandwich whose PE was processed using an Al protecting-layer. The magnitude of the surface potential increases slowly from SC/PE interface to bulk PE to reach a maximum value. Strong variation of surface potential maximum from one cross-section to another one acquired on the same sandwich is observed. However, the variation range is more important for the cross-section processed with PET protecting layer when compared to Al. This can be due to local variation in surface chemistry (cf. FTIR and PL results reported in [9]), inducing differences between cross-sections coming from different sandwich areas.

Owing to the difference between PE and SC, we would expect a sharp transition of the surface potential at interfaces instead of this “bell-like” shape. This smooth variation of surface potential may have different origins. First, a smooth transition could be the consequence of KPFM spatial resolution resulting from parasitic capacitance between AFM probe cantilever and sample [12].

To identify the impact of this factor in our experimental conditions, the surface potential profile was measured over a reference sample with Au and Al electrode deposited over silicon nitride [13].

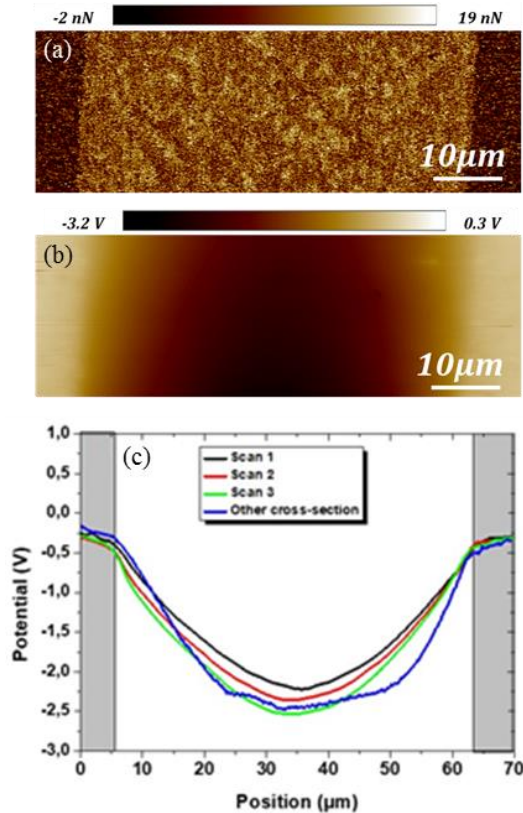


Fig. 1. Comparison of (a) adhesion, (b) surface potential map and (c) surface potential profile for sandwich whose PE was processed using Al. Grey areas in (c) represent SC and “other cross-section” corresponds to other sample (same sandwich which was cut at different position).

In this structure, the surface potential profile presents a sharp transition (2  $\mu\text{m}$  width) at Au/Si and Si/Al interface and the difference of Al and Au surface potential (1.1eV) corresponds to the difference between their work functions. This shows that even if the surface potential absolute value is unattainable under ambient conditions, relative measurements are possible. The origin of the smooth transition observed in our sample is therefore not due to the limitation in spatial resolution of the KPFM. Such smooth interface was already observed in P-N junction [14]. In this case non-abrupt interface was attributed either to doping (i.e. electric charges) [15] or material diffusion from one layer to another [16]. In our case, we can exclude diffusion of carbon black particles in the SC/PE interface as shown by the adhesion contrast in Fig. 1(a). This suggests that other sources of charges are involved in this phenomenon. A methodology to extract charge profiles from surface potential measurements has been developed to confirm this analysis.

#### B. Interface charge quantification

To determine the charge density  $\rho$  from the surface potential, we need to assume that it reproduces the bulk potential. The validity of this hypothesis was demonstrated qualitatively by Emmerich et al. [17] when charges are uniformly distributed in the volume. The charge density distribution can be obtained from the Maxwell-Gauss law:

$$\nabla \vec{D} = \nabla(\epsilon_0 \vec{E} + \vec{P})$$

where  $D$  is the electric displacement,  $\epsilon_0$  the vacuum dielectric constant,  $E$  the electric field,  $P$  the polarization.

This equation can be rewritten, inserting the potential, as:

$$\nabla^2 V = -(\rho_{\text{free}} + \rho_{\text{pol}}) / \epsilon_0$$

where  $\rho_{\text{free}}$  and  $\rho_{\text{pol}}$  stands for free and polarization charge respectively.

We intend to apply this second derivative to the KPFM surface potential map which consists of a matrix of numbers which represent the value of the surface potential in different points. To calculate the first and second differential order of the potential map shown in Fig. 1b, Savitzky-Golay smoothing method in two dimensions was implemented [18] using a third order polynomial to fit experimental data. Due to the symmetry of the sample and in order to simplify the calculation, the derivative has been calculated only across the perpendicular direction of the interfaces. Results in terms of charge density profile are presented in Fig. 2(c). Close to each interface a negative charge density cloud (free and polarization charges) is present in PE with corresponding positive image charges in the SC.



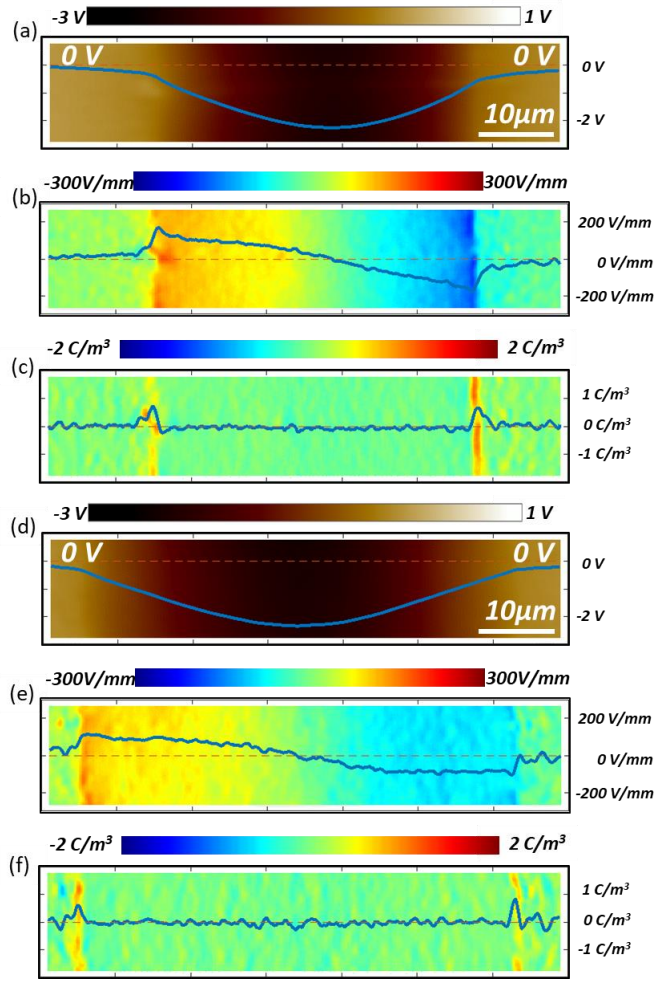


Fig.2. Comparison of surface potential, electric field, and charge density maps (top to bottom) for sandwich whose PE was processed a), b) and c) using Al, and d), e) and f) PET cover layers. The charge density is computed using Savitzky-Golay 2D method.

### C. Process influence on charge distribution

Fig. 2 depicts the electric field and charge density profiles for PET and Al as cover layers. In both cases, negative charge accumulation is seen at the PE/SC interface with its positive image charge in SC. Whatever the process, negative or positive charge clouds spread over around 2-3 μm in PE. However, the maximum density is strongly variable depending on the process.

### D. Polarization influence on the charge distribution

An external electric field was applied on PE by keeping the SC electrodes on different potentials. Two kinds of configuration are tested. In one case, the left electrode was on 2V, while the right electrode was on -2V (fig. 3(a)). In the other case the polarity was reversed (fig. 3(d)).

Fig. 3 shows the surface potential profile for the two cases. From the calculated charge density profile one concludes that negative charges are located close to the cathode and positive charges close to the anode.

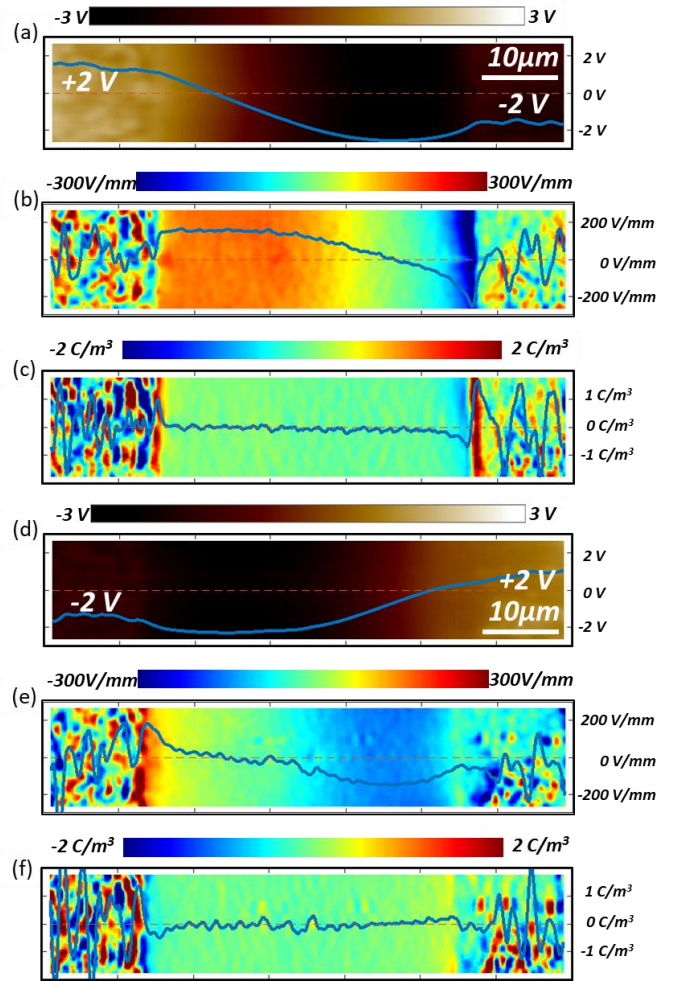


Fig.3 (a-d). Surface potential (a-b), electric field (c-d) and charge density profiles (e-f) in SC/PE/SC sandwich with PE processed with Al cover layer measured applying polarization on SC layer.

In both cases of PET/Al cover layers, charges appear within a few microns from the interface. For the Al layer a well-reproducible negative charge is observed, while for PET both polarities are detected with variation from sample to sample. This might be due to the presence of chemical species transferred to the PE surface during press molding, as revealed by infra-red and photoluminescence spectroscopy [9]. The contact charges are not affected by applying a field of a few hundred V/mm when measured after polarization.

### E. Discussion

All the samples we have tested exhibit the same sharp contrast of the adhesion force between the PE matrix and the SC. It has also been found [8] that the PE films processed with Al protecting layers exhibit higher interface roughness than the one processed with PET, consistently with our initial surface roughness conditions established before sandwich processing. No diffusion of CB from the SC into the LDPE has been observed.

Comparing adhesion and surface potential maps shows that, even if the physical interface is abrupt, the surface potential decreases comparatively slowly going from SC to PE. The potential variation is over a range of around 15  $\mu\text{m}$  and has a bell-shaped form for all types of protecting layer. The surface potential maximum varies from one cross-section to another one in the same sample, particularly for the sample prepared using PET as protecting layer. This can be due to surface chemistry changes which could be non-homogenous over the surface.

Whatever the process, negative or positive charge clouds (depending on cover layers during the molding process) spread over around 2-3  $\mu\text{m}$  in LDPE. The maximum density is strongly impacted by the fabrication process changing from  $-7 \text{ C/m}^3$  to  $0.7 \text{ C/m}^3$  for the PET layer, or, in terms of surface charge density, from  $-8$  to  $0.9 \mu\text{C/m}^2$ . This value is much lower than the value obtained theoretically for the contact charge density as estimated by Density Functional Theory in model situation [19]. This is probably due to KPFM lateral resolution which is for the best equal to 10 nm and usually around to 100 nm in atmospherically condition.

The charge density located close to interfaces is higher for PE processed with PET than with Al. This could be linked to the presence of oxidized species diffusing from the PET cover layer. However, there is a strong variation in the amount and sign of charge in the case of the PET cover layer depending on process conditions. It is not clear whether this behavior is a consequence of the interaction of the PE matter flow with PET surface during processing.

Finally, it has been found that the surface potential profile is influenced by the lateral bias applied to the SC electrode. Obviously, in this way, the initial surface potential is superposed to the linear one induced by the bias applied on the SC. This internal electric field induced by applying the dc voltage appears proportional to the applied voltage and there is no apparent evolution of the initial charge distribution under this moderate applied field (under 80 V/mm): this charge appears therefore relatively stable. As future perspective of this work, the application of higher electric fields to inject charges in LDPE will be crucial to investigate at a local scale the charge injection and to compare injected charge density determined by KPFM and PEA (Pulse Electro Acoustic) methods.

#### IV. CONCLUSION

The synergetic use of AFM-based techniques, such as PF-QNM and KPFM, has been demonstrated to represent not only a novel approach for the most complete and thorough characterization of insulating material interfaces, but also to constitute a valid method for the study of electrical phenomena at the contact, such as space charge accumulation and injection, allowing for the simultaneous correlation of the electrical properties to the physical interface characteristics, like roughness. The scatter in the results of surface potential profiles obtained by KPFM in case of PE processed with PET protective layer are suspected to be linked to the dispersion in amount of surface contamination, and, to a major extent, to the influence

of the protecting layer using in sample preparation (e.g. contamination from the protecting layer). A future continuation of this work should include the challenging task of measuring the microscopic potential after charge injection at high fields and to compare injected charge density determined by KPFM and PEA method.

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