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Barrier effect to charge injection in polyethylene by silver nanoparticles containing plasma polymer composites investigated by conductivity measurements

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***Abstract*— Main challenge in the development of HVDC polymeric insulation is to avoid the accumulation of space charge under electrical and/or thermal stresses which can significantly reduce the component reliability. Injection mitigation in low density polyethylene (LDPE) films by plasma processed silver nanoparticles (AgNPs) containing plasma polymer composites was recently reported through space charge measurements. The barrier effect has been assigned to the creation of permanent deep traps by introducing silver nanoparticles near the polyethylene surface. To substantiate the above findings, current measurements realized on composite layers and on polyethylene films with and without silver nanoparticles have been carried out. It is shown that in the presence of AgNPs in organosilicon layer, polarization/depolarization currents are one order of magnitude lower, transient currents decay faster and are not sensitive to multiple polarization. This can be understood if the AgNPs in the layer are acting as deep traps mitigating further injection with the result to decrease the apparent conductivity of the layer and to increase its breakdown strength. Similar trend is observed in polyethylene tailored by composite layer. These results strengthen the interpretation of the barrier effect based on space charge stabilized by deep traps formed by the AgNPs.**

Keywords—charge injection, injection mitigation, nanocomposite layer, thin dielectric, plasma processes

I. INTRODUCTION

Main challenge in the development of HVDC polymeric insulation is to avoid the accumulation of space charge under electrical and/or thermal stresses which can significantly reduce the component reliability [1, 2] owing to excursions in the internal electric fields beyond the design field, triggering electrical damages [3, 4]. The design of insulation for HVDC cables intended to underground or submarine energy links is one of the key points in these technologies. Cables with extruded insulation are mainly based on crosslinked polyethylene –XLPE- owing to its excellent thermomechanical stability. However, it has been realized that this well-proven technology for HVAC energy transport cannot be directly transferred to HVDC due to the presence of crosslinking residues which substantially contribute to space charge features through ionic charge build-up. For these reasons, researches developed over the recent years focus mainly on the formulation of the insulating material: strategies have been envisaged at the source of charges, e.g. through the expelling of volatile by-products, which turns out to be energetically very demanding, or through producing crosslinking processes providing substantially less amount of by-products [5]. The dispersion of nano-fillers into the polymer is another way to improve the material behavior regarding space charge features [6] although the actual mechanisms at play are not fully understood [7].

The above mentioned strategies address internal generation of charges and dissipation of available charge, but not the source of electronic carriers provided by injection at the electrodes if one refers to the electronic properties of polyethylene as a very large band gap material. Actually, only few studies focus on the polymer/electrodes interface properties to tune the charge injection effect. The most common studies consist in modification of the polymer sample interface by fluorination with a F_2/N_2 mixture [8]. Charge injection mitigation was suggested to be due to the presence of deep traps into the fluorinated layer that can block or shield further charge injection [9].

Following a strategy consisting in introducing deep permanent traps near the surface in controlled way, we have recently reported [10, 11] on a very efficient method for charge injection mitigation when a thin nanocomposite layer containing silver nanoparticles (AgNPs) is deposited on the surface of a polyethylene sample. Figure 1 shows space charge patterns obtained without and with tailored interfaces using optimized nanocomposite layers of 50 nm thickness in total. The investigated structures are with semiconducting (SC) material as electrodes, being representative of the structure in HVDC cable applications. The bulk material is low density polyethylene –LDPE-, 300µm in thickness. Whereas positive charges dominate patterns obtained on bare LDPE, no space charge build-up is detected within the bulk of the insulation, for applied fields up to 50kV/mm. The change in polarity does not affect the space charge features either. The proposed mechanism for such behavior is the ability of AgNPs to store charges, thus playing the role of permanent deep traps for the injected charges. However, as the nanocomposite layer is very

thin, it is not straightforward to sort out a precise scheme on the roles played by the plasma polymer matrix, AgNPs (size and density) and their interplay with the SC electrodes. In the following, we complete the study considering conductivity measurements achieved both on the nanocomposite layer itself and on the LDPE with tailored interfaces.

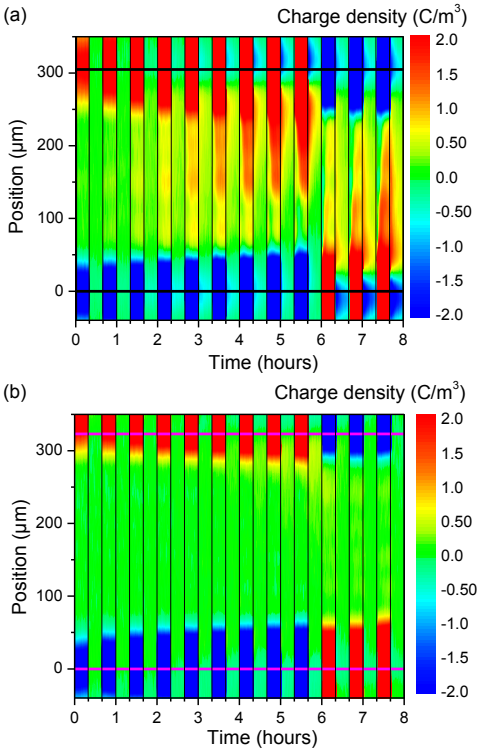


Fig. 1. Space charge patterns obtained by PEA method with volts-on/volts-off steps of 20min, for fields from 10 to 50 kV/mm in steps of 5kV/mm, followed by polarity reversal and fields of 40, 45 and 50kV/mm. SC electrodes are set at both faces. (a): reference LDPE sample; (b) two-face tailored LDPE sample.

II. EXPERIMENTS

A. *Materials processing*

The nanocomposite layer used for tailoring LDPE interfaces consists of AgNPs/SiO_xC_y:H stack. The deposition was performed in two-step process: silver sputtering to obtain the single layer of AgNPs followed by plasma polymerization to create the dielectric cover matrix [12]. For both steps, we have used an axially asymmetric RF (13.56 MHz) capacitively coupled discharge maintained at low gas pressure [13].

The results given in this work are for sputtering time of 5 s for a plasma maintained in pure argon at pressure of p = 8.0 Pa with RF power of P = 40 W which induces a self-bias voltage of V_{dc} = -725 V on the powered (smaller) electrode to perform the sputtering. The processed dielectric layer to cover the AgNPs is a plasma organosilicon deposit (SiO_xC_y:H) obtained in the same reactor with argon-hexamethyldisiloxane (HMDSO, $[CH_3]_6Si_2O$) mixture at total gas pressures of p_{tot} = 6.6 Pa and input power of P = 80 W (V_{dc} = -900 V). These plasma conditions result in deposition of large and isolated AgNPs, of 15 nm of average size and surface density of 6.1×10^{11} cm^{-2} embedded in organosilicon matrix with insulating properties of 50.0 nm total thickness to form the nanocomposite layer. Details on the structural characterization of the obtained nanocomposites are given elsewhere [10, 11].

For current measurement purposes, two kinds of substrates and structures were used:

1) heavily doped silicon substrate (R > 0.001-0.002 Ω cm, p-type, Boron doped) on which a 20 nm layer of thermal silica SiO_2 was grown in order to prevent current leakage (Fig. 2). The Si-oxidation was achieved in N_2-O_2 (1% O_2) mixture at 1100°C. Indeed, current measurements on nanocomposite layers deposited directly onto the silicon substrate provided early breakdown owing to the disordered structure of the material and the semi-insulating properties. Hence, the presented, in this contribution, current measurements were analyzed as a probe of charge build up and charge retention capability rather that as conductivity analysis. Transient current measurements obtained on the organosilicon matrix alone and on the nanostructure (AgNPs embedded in organosilicon layer) are compared. In both cases, the top electrode was a silver disc, 2 mm diameter and 150 nm in thickness, deposited by thermal evaporation.

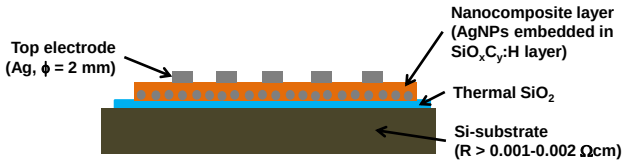


Fig. 2. Sketch of the elaborated structures on Si-substrates.

2) additive-free LDPE, 300 µm in thickness and 70 mm in diameter, processed by press-molding at 155°C [11]. The two faces of the LDPE sample were tailored with identical nanocomposite layers. Current-voltage measurements on bare LDPE and on tailored LDPE samples are compared. In both cases, SC electrodes of 30 mm diameter (and 350 µm thickness) were in contact with the sample. Prior measurement, bare LDPE was submitted to the same vacuum conditioning as for the sample with processed nanocomposite layers in order to make the comparison with equal outgassing degree.

B. *Stress protocols*

For the nanocomposite layer deposited on the Si-substrates, current measurements were carried out with a Keithley 617 ammeter using its in-built DC voltage source (up to +/- 100 V). A first protocol consisted in applying polarization/ depolarization steps of 1000 s each, applying voltages of: +0.1, 0.15, 0.23, 0.35, 0.5, 0.7, 1.0, 1.5, 2.5, 5, 7.5 and 10 V on the silver electrode (providing average applied fields to the structure in the range from 1.4 to 140 kV/mm). In a second step, we applied consecutively 16 charging/discharging cycles of 1000 V using 0.5 V applied voltage. Current was measured consecutively along the whole cycles using a 2 s dwelling time. Measurements were carried out at reduced pressure of 10 Pa at room temperature (23°C).

For measurements on LDPE substrates, a similar protocol was used. The DC voltage was provided by 12.5 kV DC supply from Fug Gmbh; current was measured through the same ammeter as above. Polarization/depolarization cycles of 1000 s were used, consistently with space charge measurement protocol. DC fields of 10, 15, 20, 26, 30 and 36 kV/mm were applied. Measurements were carried out at reduced pressure of 10 Pa at room temperature (23°C).

III. Results and Discussion

A. *Current measurements on single layers*

Fig. 3 shows examples of charging/discharging currents obtained on the structures with the Si-substrate, considering voltages of 0.5 and 1 V. This represents fields of about 10 and 20 kV/mm onto the stack. Under 1 V stress, for the sample without AgNPs (referenced S0), the charging current is still decaying after 16 min, and symmetrically, the discharging current is quite important after that time. In case of sample S1, representing the nanocomposite layer, the charging and decay clearly appear faster and the discharging current vanishes in a few minutes. When using repetitive cycles as shown in Fig. 2b, it can be observed that for sample S1 there is quickly convergence to the same shape of transient current whereas in case of S0, the current in the transient is always higher than for S1 and current progressively decays from cycle to cycle.

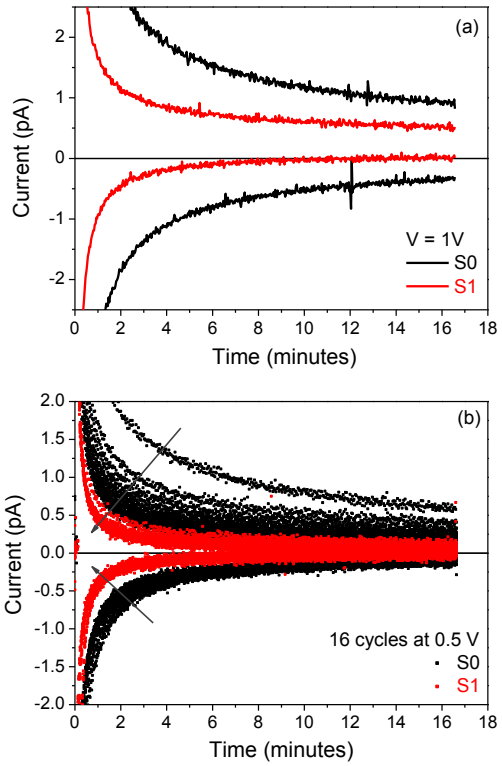


Fig. 3 Charging (positive current) and discharging (negative current transients) measured on organosilicon layers without (S0) and with (S1) AgNPs to form the nanocomposite: (a) under 1 V; (b) under consecutive steps at 0.5 V.

Finally, current-voltage characteristics of Fig. 4, obtained considering current values after 16 min charging, revealed that current in sample S1 (with AgNPs) is always lower than in S0 and that changes in the conduction regime occur beyond 10 kV/mm. In addition, early instability and breakdown-like behavior of the sample S0 occur at a field of about 50 kV/mm.

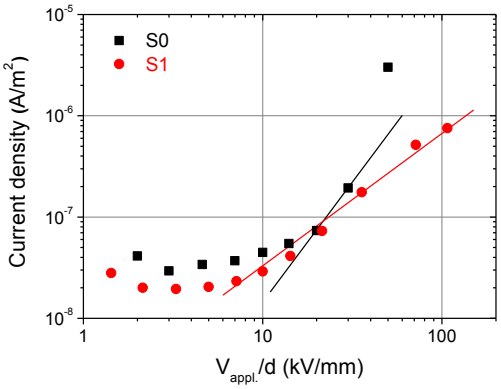


Fig. 4. Current density vs. average field measured on organosilicon layers without (S0) and with AgNPs (S1). The averaged field is estimated considering the thickness of SiO_2 and organosilicon layers.

Interpretation of the above results is not straightforward. Note that I-V measurements in SiO_2 substrate provided very small current (< 0.05 pA after 2 min) and no breakdown for voltages up to 10 kV (500 kV/mm). Therefore, the electrical response is dominated by charges generated at the top electrode. The lower current for sample S1 cannot be explained by the current flow through the AgNPs plan as this would lead to an increase of the collected current according to the configuration of the measurements. A likely interpretation, especially in regards to the difference in shape of the transient features, is that charges injected at the upper silver electrode are rapidly stored onto the AgNPs (or at the interface between AgNPs and organosilicon matrix) and therefore screan the field at the injecting electrode. The charge stays trapped on the AgNPs even during the depolarisation phase, explaining the relatively short transient in consecutive steps. In case of S0, the behaviour is dominated by the trapping/detrapping within the organosilicon layer or at the interface with the thermal SiO_2 layer.

B. *Impact of tailored interface on the apparent conductivity of LDPE.*

Fig. 5 shows the current-voltage plots obtained at room temperature for bare LDPE and for two-face tailored LDPE. In both cases, the electrode in contact with the sample is a semiconducting material, *i.e.* the same configuration as for the space charge measurement results plotted in Fig. 1. As can be observed, there is a substantial difference in the behaviour of the two samples. First, a quantitative difference, with a drop of the apparent conductivity by about one decade in the sample with tailored interfaces, in the high field range. Second, there is a qualitative difference through a change in the slope of the current-voltage characteristic from to 2 to almost 1, *i.e.* from what seems relevant from a space charge limited current to a behaviour featuring ohmic conductivity.

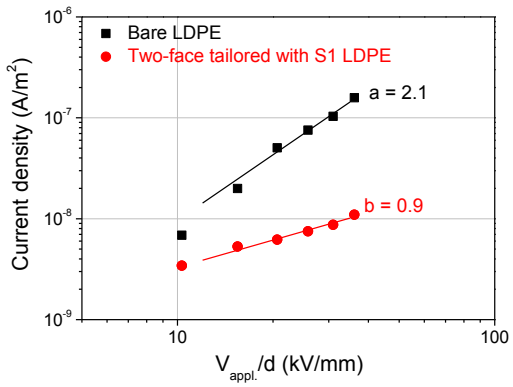


Fig. 5. Current-field plot obtained for reference LDPE and LDPE with tailored interfaces using SC electrodes. Data are relevant to charging current after 16min of polarization.

From these conductivity results, the injection mitigation effect by the tailored interfaces can be confirmed and substantiated. The SC/LDPE interface (without nanocomposite layer) provides very efficient injection, particularly for positive carriers, and also for negative carriers if compared to Aluminum electrode for example [11, 14]. In such situation, as shown in Fig. 1a, positive space charge builds up adjacent to the positively biased electrode, and an equilibrium situation is reached between the flux of injected carriers and their transport in the insulation. The injection flux is modulated by a decrease of the electrode field, a process in line with the square dependence of the conduction with field. The conduction behaviour changes drastically when the interface is tailored with the AgNPs/SiO_xC_y:H stack. With injection mitigation by forming artificial traps, the amount of carriers, whether they escape from the traps or cross the barrier due to traps saturation is substantially reduced and space charge limitation is no more at play. A field reduction at the electrode of up to 50 kV/mm can be produced with the achieved high density of AgNPs for S1, and supposing that every nanoparticle is able to accomodate at least one elementary charge. The insulating SiO_xC_y:H matrix that embeds the AgNPs ensures the storage effect by blocking the charges not to escape the AgNPs. Current results are in line with charge transport models relevant to LDPE [15] on the fact that holes appear as the dominant electronic carriers in PE. Moreover, the efficiency of the tailored interfaces was demonstrated in case of negative carriers as well (Fig. 1b) [11].

IV. CONCLUSION

Charge injection mitigation in low density polyethylene films by plasma processed AgNPs containing organosilicon plasma polymer, recently reported through space charge measurements was reconsidered in the light of charging/discharging current measurements. With the plasma mediated nanocomposite layer deposited on SiO_2 on silicon, we show a strong effect of the presence of AgNPs on the charging current and on cycling charging steps, pointing out the quick trapping of injected charges on the AgNPs. With two-face tailored LDPE layers, a strong decrease of the apparent conductivity is observed and a change in the conduction regime from space-charge limited to ohmic conduction is revealed. These results strengthen the interpretation of the barrier effect based on space charge stabilized by deep traps formed by the AgNPs embedded in insulating plasma polymer matrix.

ACKNOWLEDGMENT

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