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AC Electroluminescence spectra of Polyethylene Naphthalate: impact of the nature of electrodes

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Abstract- One of the unresolved questions in the EL spectrum of insulating materials in general is the occurrence of red emissions under AC electric field when using e.g. silver or gold as metal electrodes. Surface plasmons (SPs) effects and/or charge recombination on surface states have both been advocated as possible origins for such emissions. In this contribution, EL of 25 μ m Polyethylene 2, 6-Naphthalate (PEN) films are investigated using Indium Tin Oxide (ITO) and gold (Au) electrodes separately, the singularity of ITO being that it does not exhibit the SPs effects characteristic of noble metals (e.g. gold) in the visible domain. EL spectra and EL-field characteristics were recorded under DC and AC fields, as well as phase-resolved EL patterns. Emission spectra from ITO-PEN-ITO do not reveal the red emission contrary to that of Au-PEN-Au. Results are discussed regarding both the origin of the emissions, and the consequences that SPs-mediated emissions may have on EL features such as EL-field characteristics, spectra, and phase patterns.

I. INTRODUCTION

The electroluminescence (EL) of insulating polymers is an exciting field of research because it gives insight into electrical ageing and breakdown processes. Various physical and chemical mechanisms have been involved in the aging of electrical insulations under DC and AC stress [1,2]. Electroluminescence (EL) is a phenomenon involving physical processes such as charge injection, extraction, and transportation, but also chemical reaction through excited states. Electric fields can produce excited or ionized states, some of which have a non-zero probability for light emission during their relaxation and for chemical reaction in their excited states. Hence, on one hand, EL can be a probe of charge excitation and recombination processes, on the other hand, it may provide information on the nature of defects and luminescent sources. Because interfacial electronic states are very important in charge transfer at the electrode-dielectric interface, it should impact on the EL features, especially under AC stress. Therefore, EL can also gather information and be used to probe the physical/chemical processes occurring at the metal-dielectric interface.

Furthermore, electromagnetic properties at metal-dielectric interface undergo an increasing interest in a booming area of sciences called "plasmonics". Surface Plasmons (SPs, or more exactly Surface Plasmon Polaritons, SPPs) are electromagnetic excitations that propagate along the interface between a metal and a dielectric. It can be excited by a supply

of energy, either photon or electron irradiation on a rough (not perfectly smooth) surface [3]. Therefore, SPs effect can be expected at a dielectric/metal interfaces submitted to an electric field. For these reasons, electroluminescence phenomena observed in the red region (600-850nm) in insulating polymers with noble metal electrodes (Au, Ag) have been attributed to SP emission [4]. SP processes should not be present in indium tin oxide (ITO), a transparent conducting oxide used as electrode in electroluminescent devices.

The aim of this paper is to analyze the impact of the nature of different electrodes on electroluminescence features through EL field characteristics, spectral analysis, and phase angle analysis under AC field. In this way, the origin of the red emission should be unraveled. Polyethylene 2, 6-Naphthalate (PEN, an aromatic polyester), is particularly suitable for understanding electroluminescence in polymeric dielectrics, not only because it gives a high performance with physical, thermal, and chemical characteristics but also EL intensity of PEN under AC and DC field is relatively strong.

II. EXPERIMENTAL PROCEDURES

All the measurements were performed on PEN films of 25 μ m thickness supplied by Dupont (Dupont Teijin Films Teonex® Q51). These PEN films were metallized with ITO electrodes (thickness: 200 nm, diameter: 50 mm) and Au electrodes (thickness: 30 nm, diameter: 50 mm), respectively. Samples, sandwich structures as Au-PEN-Au and ITO-PEN-ITO, were designated.

EL experiments were performed at room temperature, under high vacuum (10^{-7} mbar) in order to avoid gaseous discharges. Light detection is carried out by two systems: a cooled photomultiplier (PM) working in photon counting mode for integral light detection, and a grating monochromator (4.5 nm in resolution) coupled to a liquid nitrogen cooled charge coupled device (CCD) camera for spectral analysis which covered the wavelength from 300 nm to 850 nm.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. EL vs. Field Characteristic

In Fig. 1, the EL and current vs. field characteristics of PEN under DC stress are plotted for different electrodes. EL vs. field of PEN under AC stress at different frequency is also shown in Fig. 2. Under DC stress, there is no significant

difference between two kinds of electrodes. The EL thresholds are both at about 160 kV/mm (though slightly lower for Au-PEN-Au). However, under AC stress, it can be seen clearly that there is an embossment for the Au-PEN-Au sample in the low field region, increasing with an increase in frequency, which does not exist in the ITO-PEN-ITO. This embossment could be eliminated from the EL spectrum of several polymers with Au electrodes using a cut-off optical filter in the red part of the spectrum [4]. This was a first indication of the existence of several contributing processes, with distinct field dependencies, to the EL of insulating polymers.

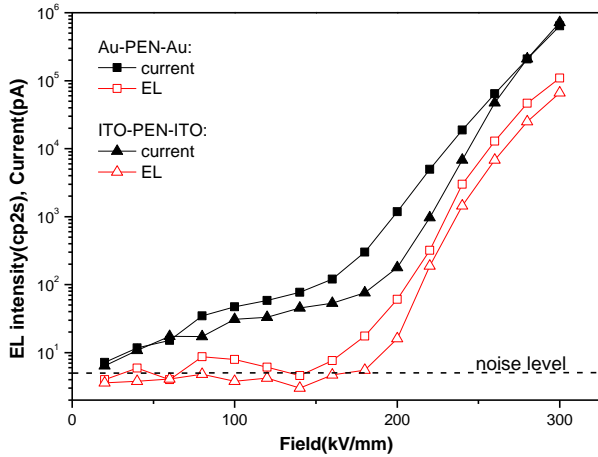


Fig. 1. Electroluminescence intensity and current vs. field characteristics of Au-PEN-Au and ITO-PEN-ITO under DC stress. The dotted line is EL noise level. "cp2s" stands for counts per 2 seconds. Data are taken after 10 min under constant voltage.

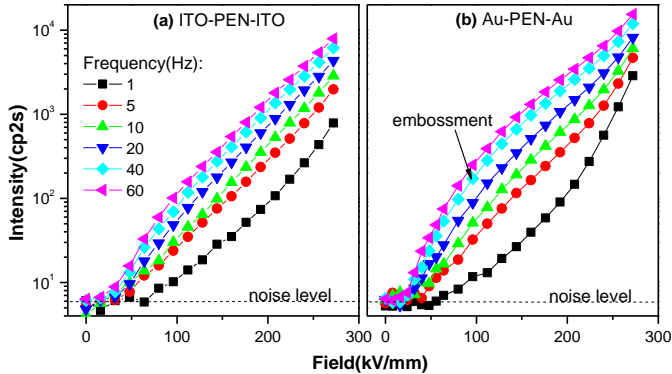


Fig. 2. Electroluminescence of (a) ITO-PEN-ITO and (b) Au-PEN-Au under AC stress. Conditions are the same with Fig. 1.

B. Spectra

The emission spectra of the PEN samples with Au or ITO electrodes are shown in Fig. 3 in order to identify and analyze the light components. The shape of the spectra is fully consistent with those reported earlier, with bands at 500, 578, 618 and 675nm [5]. In both two graphs of Fig. 3, under DC stress, normalized at 578nm, the bands at 618nm and 675nm are strengthening with the increase of the field. In the same time, the contribution of the wide band at approximately 500 nm clearly decreases. In brief, the two spectra follow the same trends with the field.

However, under AC stress as in Fig. 4, the spectra of PEN with Au and ITO electrodes are obviously different. Under low field as in Fig. 4 (a) and (b), the maximum EL intensity of the broad peak in Au-PEN-Au sample is at about 650 nm, while that of ITO-PEN-ITO sample is rather flat from 450 nm to 650 nm. The EL intensity of the former is also much stronger than the later under the same field. Hence, there exists an additional red component emission (600nm-750nm) in the Au-PEN-Au samples, which does not exist in the ITO-PEN-ITO samples and which is also not observed in both two samples under DC stress. It is tempting here to associate the emission in the red to the process at the origin of the embossment in Fig 2. From Fig. 4 (c) and (d), in the high field range, the spectra are almost the same with different electrodes, demonstrating that the red component has a higher contribution to the EL at low field.

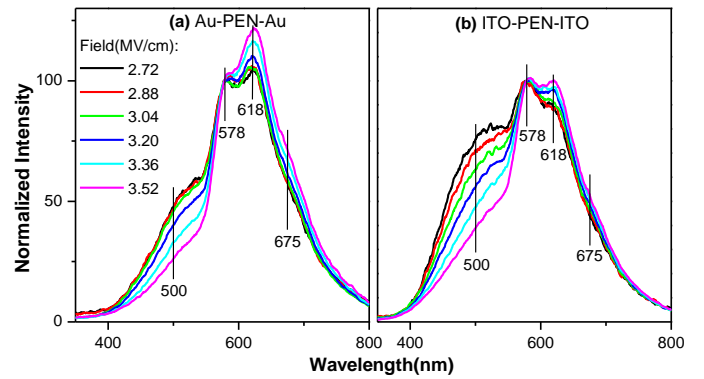


Fig. 3. Spectra of (a) Au-PEN-Au and (b) ITO-PEN-ITO under DC stress, Spectra normalized at 578nm, $EL_{578nm}=100$.

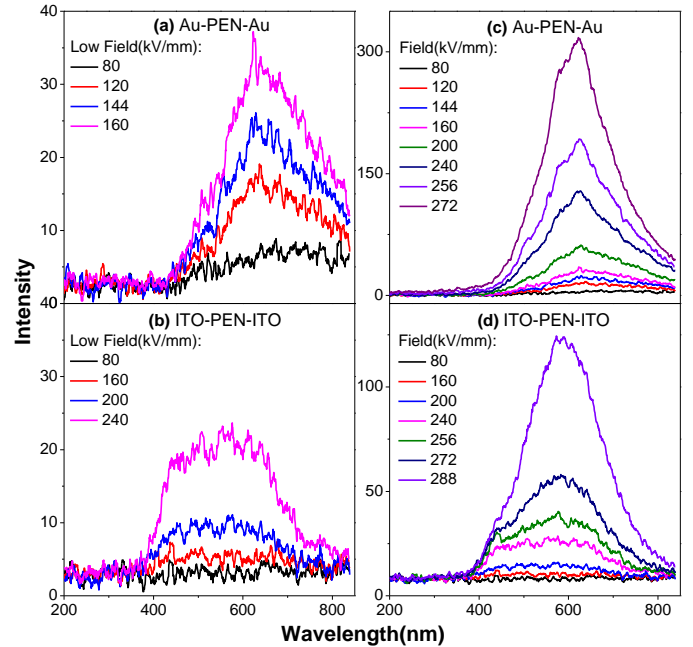


Fig. 4. EL spectra of Au-PEN-Au and ITO-PEN-ITO under AC stress, frequency: 60 Hz. Intensity is given in counts for an integration time of 5min. (a, c) Au-PEN-Au; (b, d) ITO-PEN-ITO; In (a, b), only spectra with low intensity are shown for sake of clarity.

C. Origin of the Red Component Emission

There are many experimental facts inclining for an emission process occurring at the contact of electrode/polymer under AC, due to charge injection/extraction at the interface [6]. This also explains the fact that the red component is not detected under DC because the EL comes from the bulk of the sample in that case, contrary to the AC case where charge exchange is mainly occurring at the contact. The fact that the red component is not observed with ITO electrodes under AC is another evidence that its source is located at the contact. But there are still two possibilities: either the electrodes themselves are involved in the emission process, or the interface states.

In the interface between gold and PEN, there are interface states due to structural disorder, along with possible chemical disorder due e.g. to oxidation. Both of them may lead to specific emission spectra. Under AC field, with the injection and extraction of charge carriers, these states can act as recombination centers and could emit red emission as postulated in [7]. Though the surface states of PEN metalized with Au or ITO should be almost the same, SPs in Au could produce surface enhanced luminescence [8], boosting therefore luminescence from charges recombination on surface states.

The other possibility is direct emission from SPs. Indeed, it is established that SPs, that are coherent electron oscillations can relax radiatively [9]. Along a perfectly smooth interface, the momentum k_{sp} of SPs is parallel to the interface and is always greater than the momentum k_{ph} of photons, precluding light emission from SPs (The momentum of both particles, photons and surface plasmons, must match). Along a rough interface however, SP momentum components parallel to the interface can match the momentum of photons. Therefore, SPs can radiate at a rough interface. The optical red emission due to SPs from Cu, Ag, and Au was investigated by P. Dawson et al. [10].

The surface roughness of our PEN film is shown in Fig. 5. The root mean square roughness, i.e. R_q , is 21.1nm, the average roughness, i.e. R_a , being 14.5nm, the maximum of roughness, i.e. R_{max} , being 331 nm, which should be almost the same with the roughness of electrode. The interface under study possesses different scales of roughness, providing the conditions for coupling SPs and light. More sharp tips at nanoscale may improve the light emission due to SPs.

The spectral distribution of light emitted by SPs depends on the surface roughness of electrodes itself and the energy distribution of charge injection/extraction produced by the field. Hence, the roughness of electrode surface and the field applied on it are two key factors. Under AC stress, due to alternative injection at the surface of electrodes, high density of carriers always exists here. So under AC low field, the energy distribution meets the requirement of SPs. However, under DC stress, charge injection starts, then due to screening effect, the current density of injected carriers is much less than in the AC case. The peak of current density happens in each half cycle as modeled in [11]. Hence, we consider that the red emission is mediated with SPs effect.

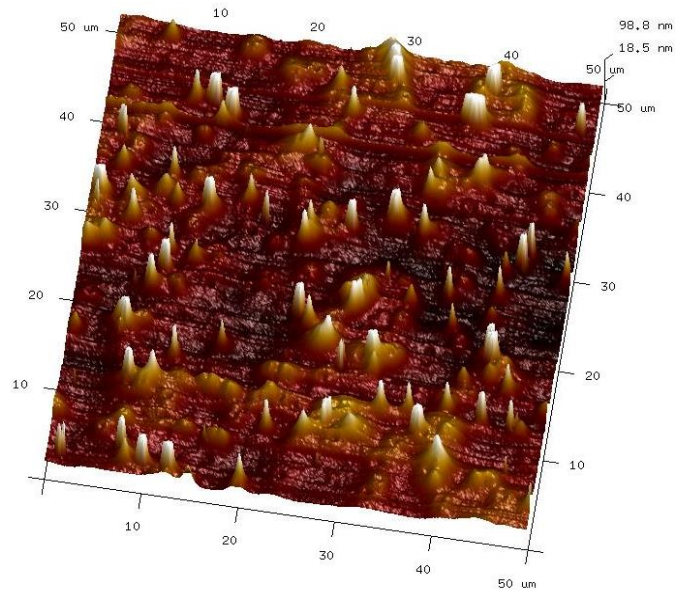


Fig. 5. Topography of a PEN film obtained by AFM. Statistics on the image are as follows: r.m.s. roughness $R_q=21.1\text{nm}$, average roughness $R_a=14.5\text{nm}$, max. amplitude $R_{max}=331\text{nm}$.

D. Phase-resolved EL

Interpretation of the EL dependence on voltage waveform can give us information on charge injection and extraction as well as transport and recombination. More importantly, it may be also influenced by the red emission component. Fig. 6 shows the phase-resolved EL patterns of PEN with the two kinds of electrodes under study for sinusoidal waveform voltage. Using a cooled photomultiplier, the counting dwell time was set suitable for phase-resolved EL measurements with 200 data points in one cycle under AC voltage waveform. The noise level is the same as in Fig. 1 and Fig. 2, and is negligible for these measuring conditions under AC.

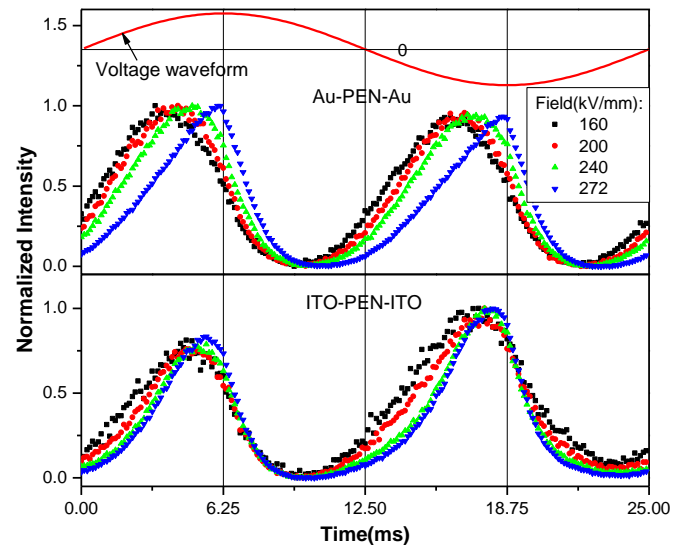


Fig. 6. Phase-resolved EL of Au-PEN-Au and ITO-PEN-ITO under AC sinusoidal waveform stress, measured at uniform frequency 40 Hz under different field. All the data are normalized at EL wave crest.

From Fig. 6, the light is emitted twice in one voltage cycle as is typical in EL experiments. In one EL cycle, EL intensity increases relatively slowly with the voltage ramping up, then it decreases more rapidly after the crest of voltage. A phase shift between the max of voltage and the max in EL is observed, which changes with the increase of the field. The EL phase angle, defined as the distance between the voltage maxima and EL wave crest are not the same for the two samples.

The average phase angles for positive and negative voltage half cycle are plotted in Fig. 7. EL phase angle of Au-PEN-Au changes drastically from 32.4 ° at low field (160 kV/mm) to 1.8 ° at high field (272 kV/mm), while that of ITO-PEN-ITO gradually decreases from 18.0 ° to 9.0 °.

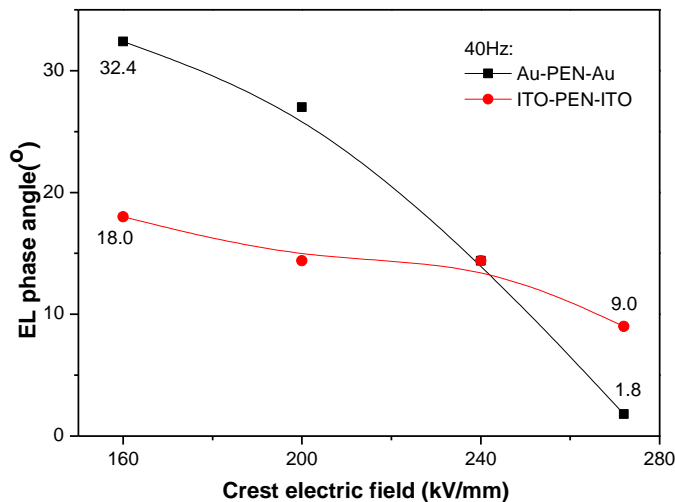


Fig. 7. Phase angle of Au-PEN-Au and ITO-PEN-ITO under AC stress.

Under AC field, injected charges either are trapped or recombine with carriers of opposite polarity trapped during the previous half cycle. EL is emitted in advance to the crest voltage because the recombination rate of carriers is at maximum there. It can be seen that EL phase angle depends on field and it also depends on electrodes. EL phase angle has also indeed some relationship with the red component emission. Given the relatively enhanced contribution of red emission at low field, the results tend to show that the phase angle of EL from SPs would be larger than that from PEN emission. Although we need more experiments to make it clear, especially using optical filters with phase detection, it seems the red component has a specific phase angle dependence vs. field.

IV. CONCLUSION

Electroluminescence characteristic and spectra under DC and AC stress have been investigated in polyethylene naphthalate (PEN) with gold and ITO electrodes. Under low AC field, an additional red emission component is revealed with Au electrode and not with ITO. The red emission is added to the original EL intensity and spectral distribution of PEN. So it may derive from a new source. We have proposed that surface plasmons at the surface of gold emit the red

emission whereas ITO electrodes cannot radiate light due to its optical properties. The roughness of electrode surface and the energy distribution of charge injection/extraction produced by the field are two key factors that should affect surface plasmons.

Phase-resolved EL is emitted twice in one AC sinusoidal waveform field cycle. EL intensity peaks are in advance of voltage maxima, the phase advance depending on the field. This is controlled by the recombination of injected carriers and trapped carriers with opposite charges. Injected charges either are trapped or recombine with trapped carriers of opposite polarity from last half field cycle, generating advance of EL crest. More interestingly, with Au electrodes the phase angle changes with field more drastically than with ITO. At the ramping region of field, the SPs-mediated red emission exists and may contribute an additional light, result in their different phase angles. This can be an indirect evidence of SPs-mediated red emission. Further work is needed to fully understand the SPs-mediated red light emitting process.

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