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Studying the Interface Between Croconic Acid Thin Films and Substrates Using a Slow Positron Beam

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Abstract. Croconic acid (CA) is the first organic ferroelectric with a spontaneous polarity in bulk samples comparable to its inorganic counterparts. As a natural extension of study, ultrathin CA films (~nm scale) were investigated to reveal ferroelectric effects in films on different substrates for their fundamental and industrial significance. However, the void defect at the interface between the film and substrate is presumed to interfere with surface effects. In this work, a non-invasive technique, a slow positron beam, coupled with Doppler broadening energy spectroscopy (DBES), is applied to study the void defects within the interfacial layer between CA films and Si and SiO₂ substrates. The effect of external electric field on defect formation is also investigated and an underlying mechanism is proposed.

INTRODUCTION

Ferroelectric materials, which are traditionally inorganic and Pb based, are widely utilized in modern electronic technology, for example in medical ultrasound sensors, high quality infrared cameras, fire, sonar, and vibration sensors, and even fuel injectors on diesel engines. Recently, Horiuchi, *et al.* discovered the first organic ferroelectric material, croconic acid (CA) with a spontaneous polarity of 20 $\mu\text{C}/\text{cm}^2$ —comparable to traditional inorganic ferroelectrics [1]. While initial efforts focused on bulk samples, the growth of ultra thin films of these materials is gaining interest since the miniaturization of electronics requires fabricating film-based devices; These also have additional potential for their development into flexible electronics.

The most direct growth method for CA thin films is physical vapor deposition (PVD), most commonly thermal evaporation. Unfortunately, thin films grown via this method are not uniform [2]. Recently, we used electric field guidance *during* evaporative growth in order to orient CA molecules, to ultimately optimize ferroelectric polarization. The resultant CA films show a significant improvement in both uniformity and surface roughness as characterized by the atomic force microscopy (AFM) [3].

As the natural extension we aim to study the interface between the thin film and the substrate. This will provide insight into the basic physics of CA film optimization as well as how films can be engineered for broader applications. There are two major thrusts to this research. First, the substrate may affect the crystal structure and change the ferroelectricity of the CA film, as reported with other organic thin films [4]. Second, the fabrication of thin electronic device requires a comprehensive understanding of the interface. To fabricate high quality ultra-thin films, the first requirement is a strong adherence of the organic material to the substrate. Such adhesion is characterized by the quantity of tiny holes at atomic scale, *i.e.* void defects, between the film and the substrate. Since these defects are localized to the interface between the film and substrate, a slow positron beam coupled with Doppler broadening energy spectroscopy (DBES) is an ideal tool to detect the void defects at the interface via profiling the film depth.

Here CA films on Si and SiO₂ were fabricated using PVD, with and without electric field guidance. AFM was used to characterize the surface properties and the slow positron beam with DBES was used to study the films and film/substrate interfaces to measure the effects of substrate choice and electric field application.

EXPERIMENTAL

The detailed description of the experimental setup, including *in situ* electric field application, can be found elsewhere [3]. The CA powder purchased from Sigma-Aldrich (St. Louis, MO) was evaporated in crucible at 130 °C under ultra high vacuum (UHV) of 2.0×10^{-7} torr. A stainless steel ring with a 0.5 cm diameter aperture was positioned roughly 1.0 cm the above the sample stage and high voltage (4.0 kV) was applied to the ring when necessary. The thickness of the growing film was monitored with a quartz microbalance (STM-2, INFICON Inc. Syracuse, NY, USA) and the deposition rate was roughly 0.6 Å/min.

The surface roughness of the sample was characterized by AFM (NT-MDT NEXT) in semi-contacting mode to avoid scratching the film surface during scanning.

The DBE spectra were acquired with the custom-built slow positron beam in the Department of Modern Physics at the University of Science and Technology of China. The six samples were measured as one batch in series under the same instrumental conditions to avoid any systematic error from the slow beam. The slow positrons counting rate was 1500 c/s and the beam diameter was <0.5 cm. Positrons were accelerated to energies between 0 – 25 keV.

RESULTS AND DISCUSSION

As mentioned previously, for a thin film, in addition to the structure of the film itself the surface and interface properties are of interest and importance due to the significant effects they can have on driving the structural and functional properties of the overall film. In the following, we will first briefly summarize our recent AFM measurements on CA film surfaces and then discuss our results on the study of the film/substrate interface made with slow positron DBES measurements.

A comparison of AFM images of CA film deposited on SiO₂ substrates, prepared with or without an *in situ* electric field, is shown in Figure 1.

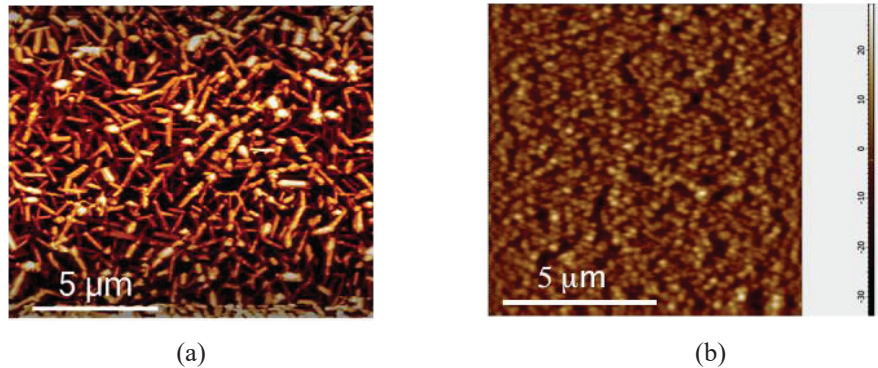


FIGURE 1. CA film prepared with no electric field applied (a) and electric field applied (b).

From the figure, it can easily be observed that the topography of the two film surfaces is very different. When grown under zero electric field, a completely disoriented haystack structure formed, where each individual needle-like feature clump may be a single crystal. This image indicates that in the absence of an electric field, and the film is mainly composed to random polycrystalline domains. Due to the orientation of the ferroelectric polarization along a preferred crystallographic axis, it is highly likely that due to the random orientations of the crystallites in this structure, zero spontaneous polarization would be observed for the film. In contrast, when grown using electric field guidance, the texture of the film surface is very different (Fig. 1b). Possible single crystal domains are evident as tiny round islands scattered on the surface and sizes of the individual islands are relatively small. This indicates that the individual ferroelectric polarizations of each island may be more easily aligned and therefore the entire film would likely have an overall higher spontaneous polarization. Since the SiO₂ substrate is insulating, the spontaneous polarization measurement cannot be obtained via hysteresis. In the future, metal substrates or bottom electrodes,

such as Au, will be used to prepare CA films allowing for a quantitative polarization measurement.

In addition to AFM used to study the surface properties of the CA films, a slow positron beam coupled with DBES was applied to characterize the film/substrate interface in order to get a better understanding of the interfacial contributions. The S parameter in DBE spectra indicates the relative concentration of defects in organic crystals like CA. It was suggested that significant amounts of positronium (Ps) are formed in the defects of CA crystals and that *ortho*-positronium (*o*-Ps) is quickly quenched due to strong pick-off annihilation [5]. The pick-off annihilation will generate 2γ irradiations and increase the counts at the center of a DBE spectrum, and hence induce a larger S parameter. Therefore, the observation of a higher S parameter indicates a higher concentration of defects in the sample. Here, this technique was used to probe defects at the film/substrate interface from samples deposited with and without electric field guidance.

The effect of the substrate on interfacial defects can be examined in Fig. 2a. The average penetration depth of the slow positrons is calculated based on the empirical equation, $z = 40 E^{1.6}/\rho$, where z is the mean depth in nm, E is the positron incident energy in keV, and ρ is the density of the film in g/cm^3 . The calculated mean depth is marked on the top of Figure 2a. From the figure, it is seen the interface reaches a depth of 500 nm. This is very consistent with the thickness obtained from the *in-situ* microbalance measurement. There are several distinct layers in the depth profile of the S parameter. First, when the incident positron energy is higher than 15 keV, positrons will completely penetrate through the oxidized SiO_2 top layer into the bulk Si (the SiO_2 substrate is fabricated as a top oxide layer on an Si wafer). This is why the S parameters are same for both samples for this energy range. Second, when the incident energy is between 6 -15 keV, the mean penetration depth of positrons is different for the two substrates, Si and SiO_2 . The S parameter for SiO_2 is lower than that for Si, which is consistent with the previous results [6]. Third, when the incident energy is lower than 6 keV, the positrons mainly stop within the CA thin film. From the figure, it is seen that at the very surface of the film, the S parameters for both samples are almost identical. Then, as positrons penetrate deeper and closer to the substrate, the difference in S parameter between the Si and SiO_2 samples increases until an incident energy of 5 keV, corresponding to the film/substrate interface. This indicates the substrate has a strong effect on the CA film deposited on it. As stated above, the S parameter is related to the concentration of defects. The lower S parameter of the CA film on SiO_2 substrate reveals a lower concentration of defects at the interface and the film. This can be interpreted by looking at the chemical structure of CA and SiO_2 as shown in Fig 2 b). The CA molecule has two –OH groups that have a tendency to form H-bonds with O atoms in SiO_2 adherence to the S. This likely leads to a higher adherence with the O_2 surface, resulting in a reduction of defects at the CA/ SiO_2 interface as compared to CA/Si.

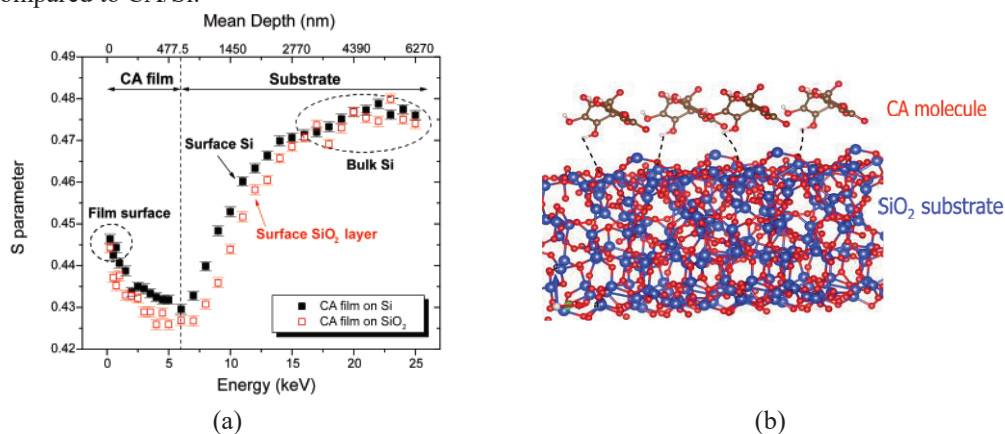


FIGURE 2. (a) DBES spectrum of CA films on Si and SiO_2 substrates. (b) Schematic diagram of CA on SiO_2 substrate.

DBES was also used to analyze the effect of electric field on the CA/substrate interface, with measurements of the S parameter shown in Figure 3. From Figure 3a, it is seen the electric field has almost no effect on the film and interfacial layer when deposited on SiO_2 substrates. This may be because the strong H-bond interaction between CA molecules and SiO_2 substrate surpasses the electric effect on the orientation of CA molecules during deposition. Hence, for SiO_2 , the application of an *in situ* electric field does not have a significant effect on defect formation at the interface. In contrast, as shown in Figure 3b, electric field has a strong effect on CA films deposited on Si. This is due to the lack of a strong interaction as the H-bond between CA molecule and Si allow CA molecules to orient easily and therefore a strong electric field applied helps CA molecules align more uniformly on the substrate

surface, reducing the formation of defects.

It is interesting to note in Figure 3b that the electric field has a stronger effect on the defect reduction in the interface layer than in the surface layer. This may be explained by same reasoning as above: in the interfacial range, CA molecules interact with Si and the relatively weak interaction between them allows the stronger effect from electric field to win out. However, in the surface layer, the CA molecules have mutual H-bonds that restrict the external effect from the electric field.

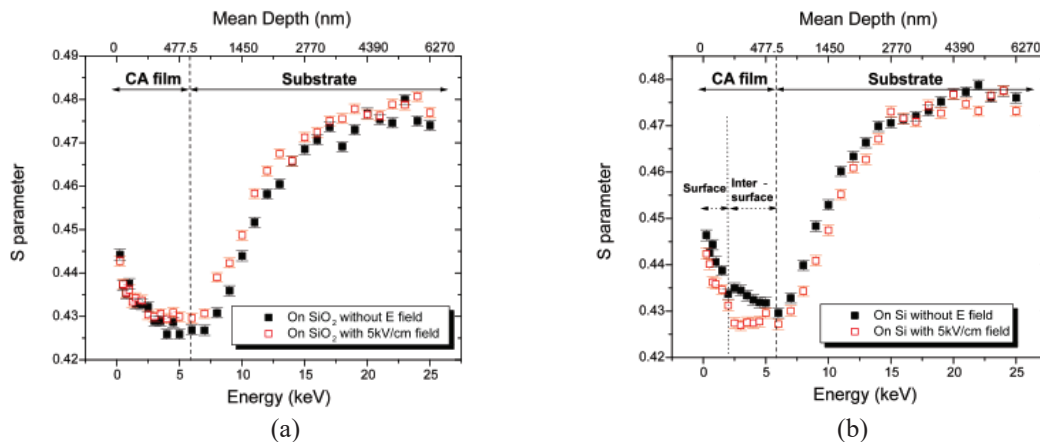


FIGURE 3. Effect of electric field on CA films on SiO₂ substrate (a) and Si substrate (b).

CONCLUSION

Thin croconic acid films were fabricated using physical vapor deposition, with or without *in situ* electric field guidance on two substrates, Si and SiO₂. The surface topography of the films was characterized via atomic force microscopy and the interfacial defect concentration of the films was studied via slow positron beam coupled with Doppler broadening energy spectroscopy. It was found that surface of the films prepared with an electric field have more uniform morphologies, indicating better molecular alignment. It was also found that the interface of the film and SiO₂ substrates has lower defect concentrations than on Si substrates. In addition, the application of an electric field during deposition significantly reduced the defect concentration in the interface of the CA film on Si with no effect observed for the SiO₂ substrate. These phenomena may be explained by strong H-bond interactions between CA molecules and SiO₂ substrate.

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