Effect of nano-SiO_2 films on the electron radiation induced conductivity of polyimide*

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The radiation induced conductivity (RIC) behaviors in nano-SiO_2 deposited polyimide (PI) were investigated using the *in situ* measurement technique. The results indicate that, by comparison with the case of virgin polyimide, the RIC in nano-SiO_2/polyimide shows low steady state values. Moreover, the steady state RIC is a power function of the dose rate with a power index of 0.659, lower than that of 0.76 in the virgin polyimide. The interfacial barrier and trapping effects are the main reasons for the change. Meanwhile, both of the interfacial effects also result in a unipolar carrier transportation mechanism in nano-SiO_2 deposited PI from the dipolar one in the virgin PI. The mechanisms of the RIC behaviors are discussed in the paper.

Keywords: polyimide, radiation induced conductivity, Nano-SiO_2

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1. Introduction

Polyimide (PI) is widely applied in spacecraft as thermal control layers and isolators of many electronic devices due to its excellent thermal stabilities and dielectric properties.[1] However, in the low Earth orbit (LEO), atomic oxygen (AO) is the most prevalent atmospheric species, which could oxidize space polymeric materials and cause serious erosion. These effects lead to performance degradations and/or even failures of polymers.[2,3] In order to prevent AO erosion, the most promising method is to deposit oxide films as a protective coating.[4–6] It is known that SiO_2 is thought of as one of the most effective AO protective coatings due to its high oxidation stability.[5–7]

Besides the AO erosion effect, under the charge particle irradiation, the charging effect should also be considered and investigated for use on spacecraft, since it can cause many anomalous behaviors.[8–12] Wertheimer and his coworkers found that thin SiO_2 films could greatly reduce the frequency of discharge events.[13] Hence, SiO_2 deposited polymers can mitigate spacecraft charging hazards.

In an ionization environment, the conductivity of the isolator could be enhanced due to the radiation induced conductivity (RIC). This phenomenon can enhance the leak current to some degree, reducing the rate of the charge accumulation. Thus, RIC becomes a very important parameter to evaluate the charging and discharging properties of dielectric materials.[14] However, the radiation induced conductive behavior in oxide deposited polymer has not been reported so far. In this paper, the radiation induced conductivity in SiO_2 deposited polyimide under the electron irradiation was investigated using an *in situ* measurement technique.

2. Experiment

2.1. Preparation

Our previous work developed a procedure for the deposition of TiO_2 thin films on glass substrates using the successive ionic layer adsorption and reaction (SILAR) method.[15] In this experiment, a similar procedure was used for nano-SiO_2 thin films deposited on polyimide. The commercial polyimide films Kapton-H (Dupont Inc, USA) with thickness of 25 μm were used as substrates. In this case, the silicon chloride ($SiCl_4$) was used as the cation ion source, which was dissolved in CCl_4 solvent with concentration of 0.01 mol/L. Correspondingly, deioned water was used as the anion source. Before deposition, the Kapton substrates were degreased successively for 10 minutes with pure acetone and ethanol, respectively. Then, the substrates were activated in ozonized air under 254-nm ultraviolet illumination for 15 minutes.

The SILAR deposition procedure was set as follows.

(i) Firstly, the cleaned and activated sample was immersed in $SiCl_4$ solution for 60 s to form a Si^{4+} ion adsorption layer on the surface of the polyimide substrate.

(ii) Secondly, the sample was dipped into pure acetone to purge the residual un-adsorbed precursor ions and then dried at 353 K in air.

(iii) Thirdly, the sample was soaked and reacted in distilled water for 60 s and dried at 353 K in the air.

The three steps mentioned above constitute one cycle, and thus, the nano-SiO_2 thin film can be deposited on the surface

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of polyimide films. Hence, in order to form the nano-SiO_2 thin film with a certain thickness, the 10 cycles of deposition were proceeded in this experiment. The thicknesses of deposited nano-SiO_2 films were measured as 20 nm using an SR500-type ellipsometer.

2.2. RIC *in situ* measurement

Figure 1 shows a sketch of the RIC *in situ* measurement system, including the electron irradiation source, the sample holder, the voltage supply, and the current measurement unit. In our case, all experimental processes were performed in a ground-based complex irradiation simulator (Ukraine, Physics Institute of Cryogenic, Ukraine Academy of Science). The electron energy and flux were set as 70 keV–140 keV and 6.25×10^{10} cm$^{-2}\cdot$s^{-1}–6.25×10^{11} cm$^{-2}\cdot$s^{-1}, respectively. The tracking process of incident electrons were calculated using a commercial Geant-4 code and the results indicate that the set-energy (70 keV–140 keV) electrons could penetrate through the 25-μm Kapton sample (including the 20-nm SiO_2 film and double Au electrode), thus the RIC could be *in situ* measured during the irradiation. The current measurements were carried out using a Keithley 6517B-type ampere meter, under 200-V bias supplied by a Keithley 2612 source meter. Before the RIC test, 100-nm Au electrodes were deposited on the double sides of sample using e-gun deposition technology (the vacuum is kept at 2×10^{-3} Pa when e-gun is working) at low rate of 1.5 nm$\cdot$s^{-1} to prevent sample heating. The RIC test procedure is similar to the method described in Ref. [14].

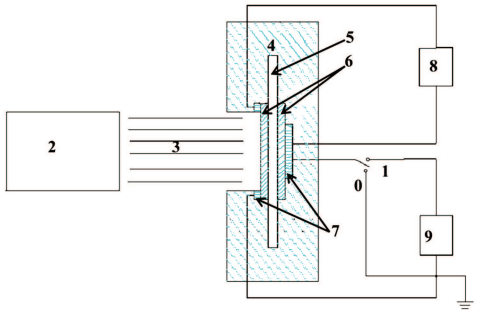


Fig. 1. (color online) Sketch of the *in situ* measurement of radiation induced conductivity, the numbers 0–9 represents the switch 0, switch 1, electron gun, electron beam, sample holder, sample, Au electrode, test contact electrode, current measurement unit, and voltage source unit, respectively.

3. Results

As a basic part of this investigation, the direct current (DC) conductivities of 20-nm SiO_2 deposited polyimide (SiO_2/PI) were measured first with the same value as about 5×10^{-17} S$\cdot$cm^{-1}, the same as that for the virgin PI. It indicates that the 20-nm SiO_2 film shows no influence on the DC electrical conductivity. This may be due to that 20-nm SiO_2 is so thin that the tunnel effect occurs under 200-V DC bias as demonstrated in some references.[16–18] Figure 2 shows the RICs of SiO_2/PI samples under the electron irradiation with various energies and fluxes. It can be seen first that the RICs in all the SiO_2/PI samples are lower than that in the virgin PI as reported in our previous work.[14] This implies that the surface nano-SiO_2 film dramatically resists the carrier transportation during the electron irradiation, regardless of the electron energy and/or flux. On the other hand, for the 140-keV electron irradiations with the flux changed from 6.25×10^{10} cm$^{-2}\cdot$s^{-1} to 6.25×10^{11} cm$^{-2}\cdot$s^{-1}, the RICs change in the same patterns as the irradiation time. It shows that as the electron beam is on, the RIC increases first to a maximum, and then decreases to a steady-state value. However, under 70-keV electron irradiation with 6.25×10^{11} cm$^{-2}\cdot$s^{-1}, the RIC increases monotonously to a steady-state value. For long-term charging process evaluation, the steady-state RIC behavior is an important parameter. Following the Rose-Fowler theory,[19,20] the steady-state RIC should be a power function of the dose rate as

$$\sigma = k\dot{R}^{\Delta}, \tag{1}$$

where σ is the measured RIC (in S$\cdot$cm^{-1}), $\dot{R}$ is the dose rate of electron irradiation (in Gy$\cdot$s^{-1}), k is a constant related to the measured material, and Δ is a power parameter, wherein Δ is related to the distribution of carrier traps with energy levels and ranges from 0.5 to 1 in magnitude. Fowler[20] pointed out that for a uniform distribution of traps with energy level, the Δ is equal to 1, and the traps should be steeply exponentially distributed with the energy level while as the Δ is equal to 0.5. In order to show the relationship between σ and $\dot{R}$, the dose rates of electron irradiations were calculated first by Geant-4 code, and the results are in Table 1. One can find that 70-eV electron with a flux of 6.250×10^{11} cm$^{-2}\cdot$s^{-1} produces a larger dose rate than the others.

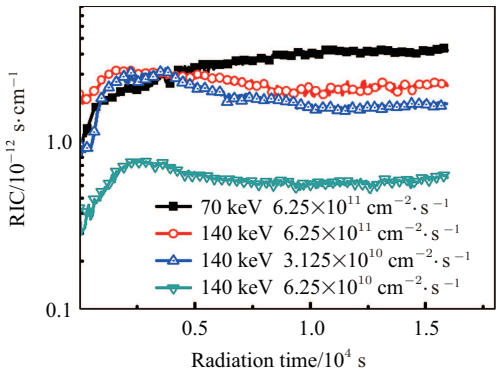


Fig. 2. (color online) Evolutions of RICs of SiO_2/PI samples under electron irradiation with various energies and fluxes.

Finally, the steady-state RIC versus the irradiation dose rate is shown in Fig. 3. The curve can be fitted following the mode of Eq. (1). In our case, the power index can be obtained as 0.659. In Fig. 3, we also shows the relationship of RIC with dose rate in the virgin PI, and the calculated power index is

0.760, larger than that of the SiO_2/PI sample. According to Fowler's rule,[20] one can deduce that, compared with the case of the virgin PI, the carrier traps show steeper distributions with energy level as the nano-SiO_2 film is deposited on PI.

Table 1. Dose rates of electro irradiation calculated by Geant-4.

Electron energy/keV	Irradiation flux/$cm^{-2}\cdot s^{-1}$	Dose rate/$Gy\cdot s^{-1}$
140	6.250×10^{10}	3.100×10^{1}
	3.125×10^{11}	1.550×10^{2}
	6.250×10^{11}	3.100×10^{2}
70	6.250×10^{11}	4.769×10^{4}

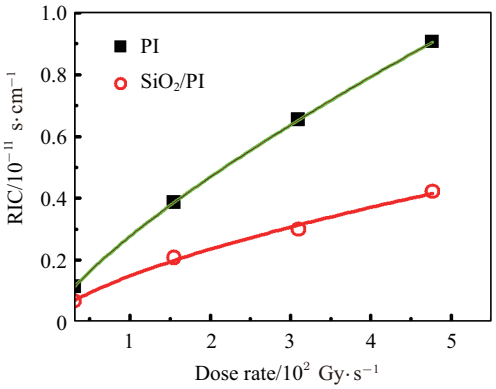


Fig. 3. (color online) Evolution of RIC with ionization dose rate in SiO_2/PI and virgin PI samples.

4. Discussion

From the above mentioned results, it is clear that the 20-nm SiO_2 film on PI can cause an obvious decrease in RIC and arise a RIC maximum when the dose rate is relatively low. It is known that SILAR deposition is performed at room temperature, implying that the process shows no effect on the structure and properties of PI substrate. On the other hand, the track simulation using Geant-4 code indicates that 20-nm SiO_2 film exerts almost no effect on the range and the dose rate of incident electrons in PI substrate due to so tiny thickness of the film. Thus, we can determine that the SiO_2 film itself and the interface between the SiO_2film and PI substrate could be the exact factors to result in the changes of RIC behaviors.

As we know that, from the structure and the property points of view, SiO_2 is a really different material from polymer-PI, namely, its conductivity as well as RIC behaviors should be different from that of PI substrate. However, in our study, 20-nm SiO_2/PI sample was detected the same static conductivity as the virgin PI due to the tunnel effect. It is reasonable to believe that, during the electron irradiation, the tunnel current can also be on and pass through the surface nano-SiO_2 film as 200-V bias-on. This implies that the surface SiO_2 film shows little effect on the RIC behaviors. In this case, the interface effects between the SiO_2 film and the PI substrate should be dominant factors to control RIC behaviors in SiO_2/PI composite samples.

As to the SiO_2/PI interface, there may be two options to exert effects on the RIC behaviors of the sample, namely the image potential and the interfacial states. On the one hand, an image potential could be built once the interface is formed between the SiO_2 film and the PI substrate, due to the completely different structure and the compositions of surface film and the substrate. During the electron irradiation, a large amount of carriers (electrons and holes) would be produced in the bulk substrate PI due to ionization effects. As the bias is on, the carriers would be redistributed to transport to the anode and cathode contacts, respectively, forming the radiation induced current. However, as the nano-SiO_2 film is deposited on PI, an electric field is formed due to the interfacial image potential effect. This image potential is attractive for both the positive and negative charges,[21] resulting in a drastic decrease of carriers, so as to the radiation induced current.

Secondly, it is understandable that there exist many hanging bonds and other bond defects within the interface region of SiO_2/PI. During the irradiation, the hanging bonds and other kinds of defects would form interfacial static traps, becoming the recombination centers of carriers (electrons and holes). In our previous investigation, it was found that during the irradiation, there was a large concentration of free radicals formed and accumulated in the interfacial region, forming a large amount of interfacial static defects. This effect may also reduce the carrier transportation efficient, becoming another reason to decrease the sample RIC as the SiO_2 film is deposited on PI.

Accordingly, the appearance of a maximum in the RIC evolution should originate directly from the interfacial effect of SiO_2/PI. From the above mentioned discussions, the interfacial states generated there come from the accumulated radicals in the SiO_2/PI interface during the electron irradiation. These two phenomena imply that the interfacial states should be traps of the hole carriers due to the negative feature of radicals. It means that there may have a unipolar conductive mode for RIC behaviors in SiO_2/PI samples. Based on the Fowler-Rose-Vaisberg model, Tyutnev and his coworkers[22] made a comparison of dipolar RIC behaviors with the traditional unipolar one in theory. Their results suggested that, in the case of unipolar conductivity, there existed a clearly decay process after the RIC increased to a maximum value as the radiation was on. While in the dipolar conductive materials, the RIC showed evolutions in a monotonous mode with the irradiation time without the maximum appearing. The corresponding results are shown in Fig. 4. Actually, the unipolar conductivity could be observed in many polymers, such as polystyrene (PS), low-density polyethylene (LDPE), polyvinylcarbazole (PVK), and polyethylene terephthalate (PET), as reported in Refs. [23]–[25]. Our previous work demonstrated that during the electron irradiation, the

RIC of the virgin polyimide increased monotonously with time up to a steady-state value.[14] This indicates that for virgin polyimide films, the carrier transportation proceeds in a dipolar mode. Comparatively, when the nano-SiO_2 film was deposited on PI substrates, the RIC increases to a maximum and then decays to the corresponding steady-state value with the irradiation time. It is clear that the hole conductivity was restricted by the interfacial traps. However, under 70-keV electron with flux of 6.25×10^{11} $cm^{-2} \cdot s^{-1}$, the RIC maximum seems to disappear, this may be due to its high dose rate. In Table 1, it is calculated that the dose rate in this case is 4.769×10^2 $Gy \cdot s^{-1}$, much larger than the others. In this case, the electron–hole pairs would be excited and formed in a relative high rate, while the interfacial trapping rate was limited due to the limitation of interfacial volume and certain temperature during the test. It means that there is a high limitation of the dose rate to cause unipolar conducting in SiO_2/PI materials.

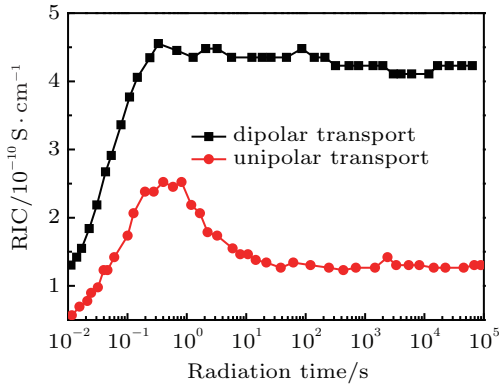


Fig. 4. (color online) Sketch of simulation results based on Tyutnev's method[22] of RIC controlled by the mechanisms of dipolar transport and unipolar transport in polymer.

5. Summary

In this paper, the evolutions of the RIC in nano-SiO_2 deposited polyimide films using SILAR method were investigated by *in situ* measurement technique. The results indicate that the RIC in SiO_2/PI is reduced compared with that in the virgin PI sample. Moreover, the evolution of RIC with radiation time in nano-SiO_2/PI has two different modes, and depend on the irradiation dose rate. Under low dose rate irradiation, the RIC increases to a maximum value with irradiation time, and then decreases to a steady state value. The second mode, appearing in the case of high dose rate (4.769×10^2 $Gy \cdot s^{-1}$), is similar to that in virgin polyimide, which shows that the RIC increases directly to a steady state. The steady state value increases with the dose rate in a power law mode with a power index of 0.659. It indicates that the nano-SiO_2 modified films result in a steeper distribution with energy level of carrier traps in the sample than that of the virgin PI. Further analysis shows that, the interface states and the image potential appearing at the interface between nano-SiO_2 and PI substrate should be responsible for the changes of RIC behaviors as compared with PI. Moreover, the effects of interface state on the RIC could be affected by radiation dose rate. Under low ionization dose rate irradiation, interfacial effects would result in a unipolar conducting in SiO_2/PI from the counterpart dipolar one in PI. However, for the high ionization dose rate, due to the limitation of interfacial trapping rate, the mechanism of RIC could return to dipolar transport.

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