JOURNAL OF MATERIALS SCIENCES 33 (1998) 4105–4109

Study on electrical characteristics of fluorinated polyimide film

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The electrical characteristics (*I–V* and *I–t*) of fluorinated polyimide dielectric films were measured as function of time, electric field and sample temperature and the results were discussed in view of existing conduction and charge-transport mechanisms. Experiments and analysis to elucidate conduction mechanisms at low and high electric fields were carried out. The results are presented and discussed. It is concluded that the bulk-limited Pool–Frenkel conduction mechanism is likely to dominate for the steady state current at high electric field above 1 MV cm^{-1}, and in the range of low electric field below 1 MV cm^{-1}, the Ohmic conduction is the main conduction mechanism.

1. Introduction

Low dielectric constant materials are required as an interlayer dielectric (ILD) in the high-density multilevel interconnection to reduce the *RC* (resistance × capacitance) delay [1, 2]. In our study, fluorinated polyimide was investigated as an ILD material. For ILD applications, low dielectric constant, high dielectric breakdown strength, and low leakage current (d.c. conduction) are necessary in addition to processing and reliability requirements [3]. Previous experiments show that the polyimide film has 2.4 dielectric constant and a $\sim$ 3 MV cm^{-1} breakdown strength. However, the leakage current conduction behaviour and mechanism were not reported. In the present work, the current conduction in this polyimide film was investigated. The measurements were carried out on metal–polyimide–metal (MPM) capacitor structure with current–voltage (*I–V*) and current–time (*I–t*) methods in the temperature range 25–200 °C at electrical field range up to 2 MV cm^{-1}. The results will be presented and discussed. A current conduction mechanism will be established and it will be shown that the polymer under investigation does qualify for ILD applications as far as electrical characteristics are concerned.

2. Experimental procedure

A schematic diagram of metal dot electrode (gate) structure for d.c. conduction measurements and a cross-sectional view are shown in Fig. 1. Samples were all prepared from p-type $\langle 1\,0\,0 \rangle$, 3 in ($\sim$ 7.62 cm) silicon wafer with intrinsic resistivity in the range 10–20 Ωcm. The lower electrode is flat, while the upper metal electrode is patterned with a shadow mask with various areas. The electrical test structure of the fluorinated polyimide film therefore is a metal–fluorinated polyimide–metal (MPM) structure. The lower electrode is connected to a current meter and then grounded, while the upper dots are directly connected to a voltage supply. On the cleaned wafer with buffered HF (10 : 1), the lower copper layer is deposited by sputtering. Copper on the substrate is annealed at 450 °C to produce a metallurgically stable structure. The fluorinated polyimide precursor is spun on to the copper-coated substrate and soft baked at 250 °C for 1 h and then hard baked at 350 °C for 1 h in a nitrogen ambient for complete imidization. Finally, the top surface contact to the fluorinated polyimide film is achieved with copper-sputtered dots. The MPM capacitor was then annealed at a temperature of 425 °C. The electrical measurements were made in a shielded, light-tight test station in the temperature range 50–250 °C in nitrogen ambient. The probe station is housed in a metal box which protects the sample from room light during measurement to prevent possible photoelectric conduction. The *I–V* and *I–t* measurements are performed by using a HP-4140B picoammeter and voltage source.

3. Results and discussion

3.1. Conductivity of the polyimide film at room temperature

The specific electrical conductivity of the polyimide is found to be around $\sim 10^{16}\ \Omega^{-1}\text{cm}^{-1}$ at room temperature and shows the exponential function of the temperature. The conductivity was calculated by

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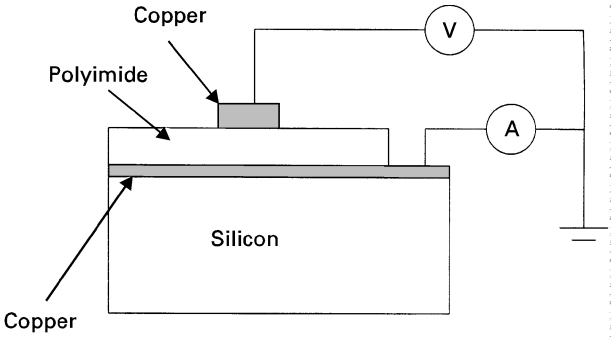

Figure 1 A schematic diagram of the metal dot electrode structure for d.c. conduction measurements.

measuring the current flow through a piece of the polyimide film as follows

$$\sigma = (d/AV)\, I \tag{1}$$

where d (cm) is the sample thickness, A is its area (cm^2), V is the potential across the materials and I is the observed steady state current. The other form of conductivity can be expressed as

$$\sigma = \sum_i q_i n_i \mu_i \tag{2}$$

where n_i is the charge carrier density (cm^{-3}) and μ_i is the charge carrier mobility ($cm^2\, V^{-1}\, s^{-1}$). Inserting the values of the conductivity ($10^{-16}\ \Omega^{-1}\ cm^{-1}$) and the mobility ($\sim 10^2\ cm^2\ V^{-1}\ s^{-1}$) into the above equation, the number of the charge carrier contributing the electrical conduction was found to be $\sim 10\ cm^{-3}$.

Next, we need to find out where the charge carriers come from. First, consider the case when the charge is only supplied by an intrinsic band transition from the valence band to the conduction band, because the conductivity of the polyimide film has been shown to increase exponentially with increasing temperature, implying that the charge carriers and the generation step are intrinsic to the polyimide. For a material with 10^{22} atoms cm^{-3} and the forbidden band gap of 2.0 eV (average value of polymeric materials), there are 10^{-4} charge carriers per cm^3 at 25 °C in the conduction band, which is significantly lower than the calculated density of the charge carriers in the polyimide film.

Consequently, the exponential relationship between the conductivity and temperature is related to the charge carrier generation, not only due to the intrinsic band transition, but also to some other thermally activated processes. Therefore, we look beyond intrinsic generation for the origin of the charge carriers for the polyimide films, such as electrode effects (Schottky effects), Pool–Frenkel effects, or ionic conduction and so on. These effects on the origin of the charge carrier and leakage current conduction will be discussed later.

3.2. Time-dependent leakage current

During the leakage current–voltage measurement, it was observed that the leakage current decreased with time after first applying the voltage, particularly for a leakage current level $< 10^{-10}$ A. A typical leakage current versus bias time is shown in Fig. 2 for 350 nm thick polyimide film after applying 1 MV cm^{-1} electric field at room temperature. All experiments were continued for a time period long enough to reach a steady state current. The currents were seen to decrease initially and then reach a time-independent value after extended exposure with the required exposure time. This phenomenon has also been observed for polyimide film by several other research groups [4, 5]. This change in time dependence suggests the initial and later current are due to different conduction mechanisms. The temporal decay of the currents is probably due to displacement current, absorption current caused by the dipole orientation, electron traps at the metal interface, and charge accumulation in the vicinity of the electrode, caused by internal charge drifts, resulting in a decrease of the effective electric field in the bulk of the sample.

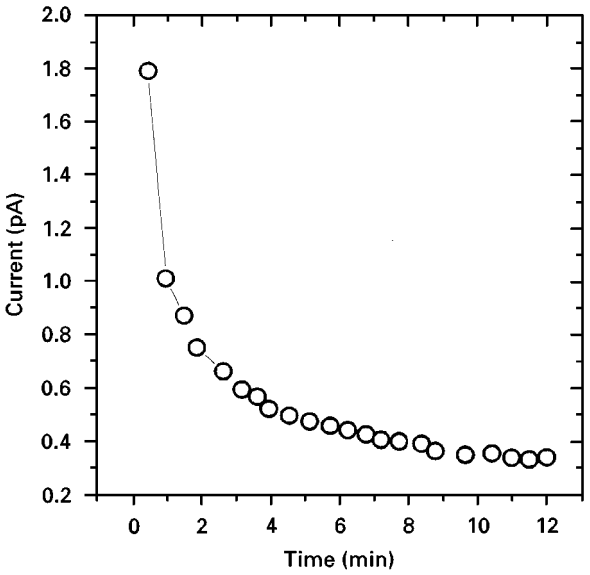

Figure 2 Current (I)–time (t) characteristics at room temperature with a 1 MV cm^{-1} electric field.

If the decrease in the current with time is due to the absorption current caused by the dipole orientation, the time to reach the steady state current is expected to be the same, independently of applied electric field because its relaxation time is usually independent of electric field. However, this is not our case. A higher electric field gives a shorter time to reach the steady state current. The observed decay is, therefore, not due to the dipole orientation, but is caused by a process having a non-linear dependence on the electric field, which is probably related to the electric conduction process.

3.3. Leakage current versus temperature

Fig. 3 shows Arrhenius plots for the steady state (constant or minimum) current versus temperature at different applied electric fields. All data points are averages of two or more measurements. It was observed that the steady-state current is an exponential function of temperature beyond 150 °C. The

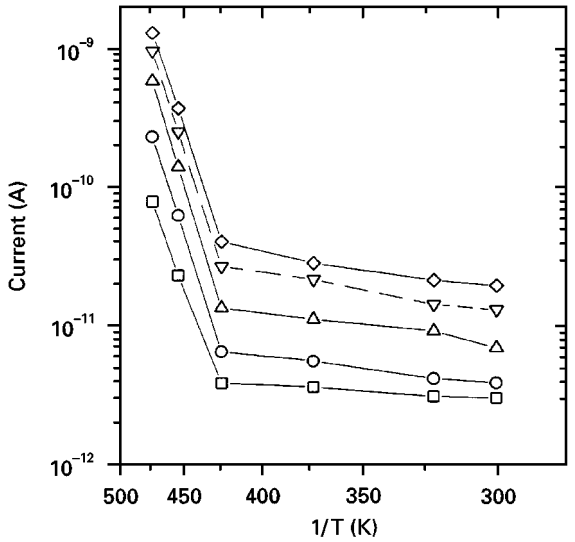

Figure 3 Arrhenius plot for leakage current versus temperature. (□) 1 MV cm^{-1}, (○) 1.25 MV cm^{-1}, (△) 1.5 MV cm^{-1}, (▽) 1.75 MV cm^{-1}, (◇) 2 MV cm^{-1}.

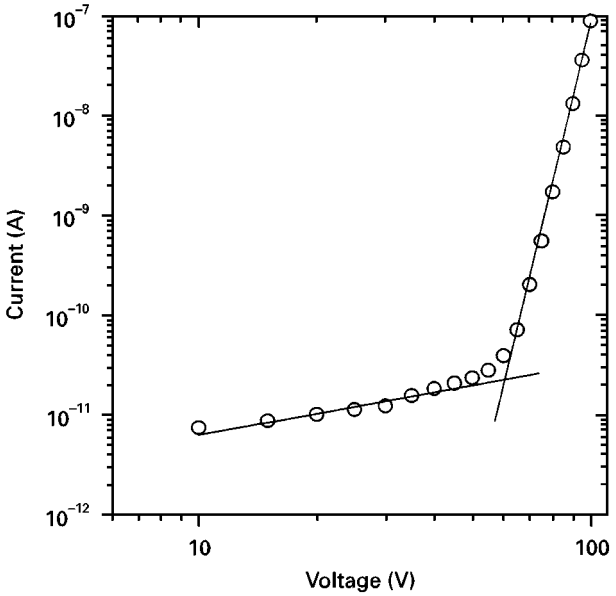

Figure 4 Voltage dependence of leakage current in the form of a log *I*–log *V* plot.

activation energy was calculated to be around 1.34 eV above 150 °C, regardless of the applied electric fields, indicating that the current conduction behaviour and mechanism are the same within the applied electric field range (1–3 MV cm^{-1}).

As shown in Fig. 3, the leakage current slowly increases up to 150 °C sample temperature, and then a dramatic increase is observed above 150 °C. This dramatic increase is probably due to the structural transition in polyimide film above 150 °C or the fact that the value of the leakage current below 150 °C is probably not a steady state current, but a transient current, because it usually takes a longer time to reach a steady state current at a low temperature (below 150 °C) than at a high temperature (above 150 °C). It was reported that the fluorinated polyimide has β-structural transition at 150 °C where side-group rotation and short-range movement of molecules are occurring [6]. In addition, *Seanor* [7] showed that the onset of molecular motion increases the conductivity of the polyimide by helping the charge carriers to escape from and transport to localized states such as surface and bulk dipole states, molecular ion states, impurities, chain ends and branches, and crystalline–amorphous boundaries [8].

3.4. Model fitting of the experimental *I–V* data

Fig. 4 shows the dependence of the leakage current on the applied voltage at room temperature in the form of log *I* against long *V*. In the low electric field ranges below about 1 MV cm^{-1}, the log *I*–log *V* plot displays on Ohmic behaviour (the slope is ≈ 1), being consistent with results reported by other groups. On the other hand, in the high electric field range above about 1 MV cm^{-1}, it deviates from Ohmic behaviour, and increases non-linearly with *V*. Several conduction mechanisms [9] such as the Schottky effect, the Pool–Frenkel effect, thermally assisted tunnelling (Fowler–Nordheim effect), ionic current, and space-charge limited current are examined to explain the non-linear dependence of the current on voltage at high electric fields. Among those conduction mechanisms, the Fowler–Nordheim tunnelling conduction mechanism will not be considered because the film thickness is much thicker (≈ 400 nm) for applying the Fowler-Nordheim tunnelling conduction mechanism (≈ 10 nm).

The fit of the present results to either Schottky or Pool–Frenkel type conduction, based on the electronic process, was examined because it was postulated by Hanscomb *et al.* [4] Considering the Schottky-type conduction, the charge carrier generation involves electron emission from a metal electrode. The electron injection from the metal electrode into the dielectric is controlled by the relation

$$J = A^* T^2 \exp\left(\frac{-q\Phi_B}{kT} + \frac{aV^{1/2}}{T}\right) \qquad (3)$$

where A^* is the effective Richardson constant, a is $(q/4\pi K\varepsilon_0 d)^{1/2}$, Φ_B is the barrier height or the effective work function between the Fermi level of the metal and the conduction band of the dielectric, K is the dielectric constant of the dielectric, ε_0 is the permittivity of free space, and d is the thickness of the dielectric. A Schottky plot of the current data as a function of the field (log I versus $E^{1/2}$) is shown in Fig. 5. The results for high fields are reasonably well represented by straight lines, while the data for low fields deviate from the straight line. The value of the dielectric constant evaluated from the slopes of the straight lines is 0.65 which is physically meaningless. Therefore, it is unlikely that the observed current is due to Schottky-type conduction.

The exponential dependence of current on $E^{1/2}$ is not only characteristic of Schottky conduction but also Pool–Frenkel conduction. If the charge carrier becomes trapped in a coulombic potential well, then

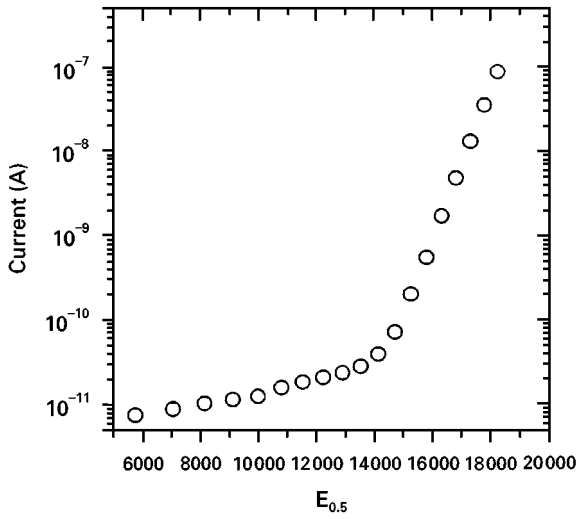

Figure 5 Voltage dependence of leakage current in the form of a log I versus $E^{1/2}$ plot.

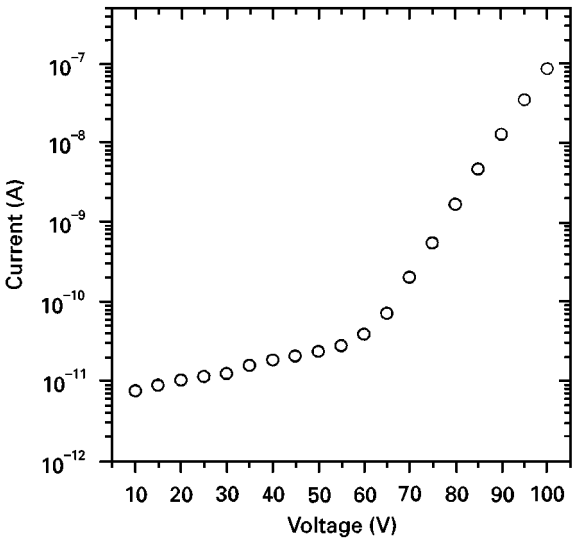

Figure 6 Voltage dependence of leakage current in the form of a log I–V plot.

field-induced lowering of the barrier to detrapping (Pool–Frenkel mechanism) has a functional dependence ($\log I/E$ versus $E^{1/2}$). In the case of the Pool–Frenkel effect, the emitted current is due to the thermal excitation of trapped electrons into the conduction band which is enhanced by an external field. The electrons can be trapped in localized states in the bulk of the polyimide film, such as surface and bulk dipole states, molecular ion states, impurities (different chemical groups, polar group, ionic groups), chain ends, branches and folds, and the crystalline-amorphous boundary, and so on. For trap states with coulombic potentials, the expression is virtually identical to that of the Schottky emission. The barrier height is the depth of the trap potential well, and the quantity $(q/\pi K\varepsilon_0)^{1/2}$ is larger than in the case of Schottky emission by the factor of 2, because the barrier lowering is twice that due to the immobility of positive charge. The value of the dielectric constant obtained from the slope of the data at high electric field is ≈ 2.6, which is consistent with the dielectric constant obtained by 1 MHz C–V measurements as well as that calculated from the value of the refractive index measured by ellipsometry. Therefore, at high electric field, the Pool–Frenkel mechanism is likely to dominate.

In the case of the ionic hopping conduction, the current is given as

$$I = I_0 \exp \frac{aqV}{2kT} \tag{4}$$

where a is the ionic jumping distance, q is the charge of the ion, T is the temperature, and k is the Boltzmann constant. The slope of the $\log I$ versus V plot would therefore give the ionic jump distance a. Therefore, the results are replotted in the form of log I versus V as shown in Fig. 6 for various electric fields. As can be seen in this figure, these plots can be regarded as a straight line. The jumping distances were calculated from the slope to be around 25 nm. As the ionic conduction requires mass transport, and hence open channels, in the materials, it is extremely sensitive to variations in fabrication. Because charge transport is due to a finite number of charge carriers initially present, the current density may be observed to decrease rapidly as several coulombs are passed through the sample and the supply of carriers is depleted. Therefore, it is thought that the basic conduction process is reflected more directly in the current observed at an earlier time rather than at a later stage.

In the case of space-charge limited conduction, the I–V characteristic in a trap-free dielectric is characterized by the current density

$$J = \frac{9\mu K\varepsilon_0}{8}\frac{V^2}{d^3} \tag{5}$$

where μ is the carrier mobility, V is the applied voltage, and d is the thickness of the dielectric. The space-charge limited current results from a carrier injected into the dielectric, where no compensating charge is present. The current for the trap-free case is proportional to the square of the applied voltage. The fit of the present results to space-charge limited conduction was examined. A plot of current data as a function of the field (I versus E^2) is shown in Fig. 7. The results for high fields are not represented by straight lines. Therefore, it is unlikely that the observed current is due to space-charge limited conduction.

3.5. Bulk-limited versus surface-limited conduction mechanism (Schottky versus Pool–Frenkel effect)

Even though these two electric field-induced conduction mechanisms are very similar to each other, the source of charge carriers differs. The Schottky effect is an electrode effect, which means that the charge carriers come from the metal electrode. However, the Pool–Frenkel effect is a bulk effect in which the charge carriers come from the bulk of the insulator. The difference between the Schottky and Pool–Frenkel

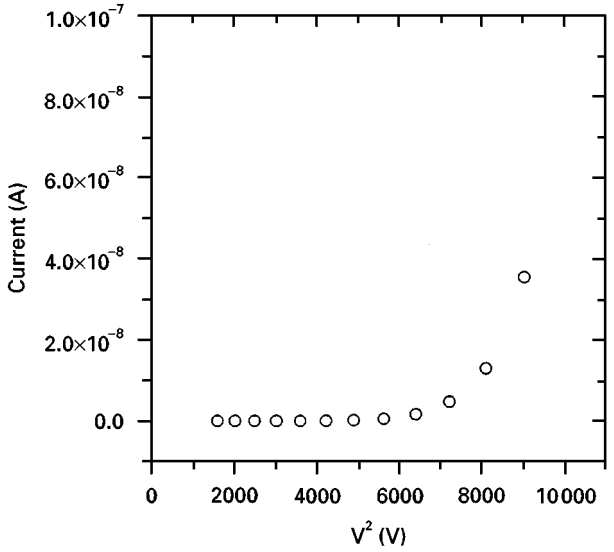

Figure 7 Voltage dependence of leakage current in the form of an I versus V^2 plot.

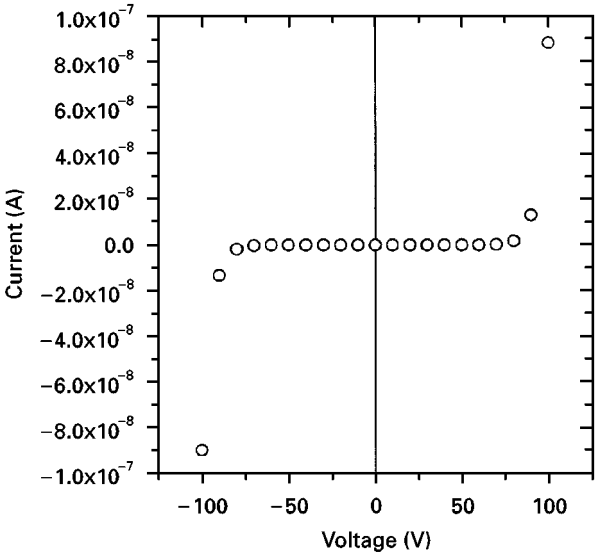

Figure 8 I–V characteristics at room temperature with applied electric field (negative to positive).

effects can be distinguished with a MIM capacitor with two metals having different work functions. The Schottky barrier is caused by Fermi-level pinning at the surface when a metal is in contact with a dielectric. By using two metals with different Fermi levels in contact with the dielectric, the conduction band edge of the dielectric is tilted due to the Fermi-level pinning at the surface. The tilting of the dielectric band edge will cause the leakage current with forward bias of the dielectric to be different from the reverse bias. A copper/polyimide/aluminium capacitor was built to test the possible Schottky effect. The Fermi level in contact with an insulator is 4.1 eV for aluminium 4.7 eV for copper, which will result in a several orders of magnitude of leakage current change when reversing the bias polarity if, indeed, the conduction is controlled by the Schottky effect. Fig. 8 shows the I–V characteristic of the polyimide film on the copper/polyimide/aluminium capacitor. It is observed that the bias polarity reverse did not yield any significant change in the leakage current of the polyimide film. This indicates that the electric field-induced conduction of the polyimide film is through a bulk-limited Pool-Frenkel process.

4. Conclusion

The electrical conduction current of fluorinated polyimide film is measured as function of time, electric field and sample temperature. The experimental curves were fitted to the theoretical curves for several conduction mechanisms. Comparing the polyimide film properties with the parameter (dielectric constant, jumping distance, etc.) obtained from the curve fitting, the bulk limited Pool–Frenkel conduction mechanism is likely to dominate for the steady-state current at high electric field above 1 MV cm^{-1}. In the range of low electric field below 1 MV cm^{-1}, the Ohmic conduction is the main conduction mechanism.

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Received 20 October 1997
and accepted 15 May 1998