Electrical Properties of Organic Materials as Low Dielectric Constant Materials

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ABSTRACT

The bonding structure of organic materials such as fluorinated amorphous carbon films was classified into two types due to the chemical shifts. The electrical properties of fluorinated amorphous carbon films also showed very different effect of two types notwithstanding a very little difference. Fluorinated amorphous carbon films with the cross-link breakage structure existed large leakage current resulting from effect of the electron tunneling. Increasing the cation due to the electron-deficient group increased the barrier height of the films with the cross-link amorphous structure, therefore the electric characteristic of the final materials with low dielectric constant was also improved. The lowest dielectric constant is 2.3 at the sample with the cross-link amorphous structure.

1. Introduction

To produce high-density, high-speed integrated circuits, a low dielectric constant (low-k) material is used to reduce the signal propagation delay time, cross-talk noise between metal layers, and power consumption [1-6]. Recent research has focused on the preparation of porous materials by spin-on coating and CVD. Promising porous low dielectric constant (low-k) materials as alternatives to SiO_2 are methylsilsesquioxane (MSQ), and organic-inorganic hybrid silica materials [7-8]. The dielectric constant of porous materials is reduced by their porosity and low ionic polarization. Organosilicate films made from bistrimethylsilylmethane (BTMSM) can be categorized as having organic, hybrid, or inorganic properties [9-11].

In organosilicate films with organic properties, the incorporation of electron-releasing groups or space-occupying groups as alkyl groups increases the free volume within the silicate network, and the porosity of the films can be predicted approximately using the Bruggeman effective medium approximation (EMA) model. The simple EMA model assumes that there are two components, such as the material forming the solid wall and voids.

Organosilicate films with hybrid properties are flatter than those with any other properties. However, organic materials have significant integration problems, such as poor adhesion and flatness. Another organic type material is fluorinated amorphous carbon (a-C:F) films which is displayed the chemical shift [12, 13]. The origin of the chemical shift seen in carbon-centered systems, such as organosilicate films, has been analyzed by considering the bonding structure of the films [14]. The hybrid properties of organosilicate films are traditionally associated with classical hydrogen bonds, such as the red shift due to elongation of the C-H bond. However, an electron-releasing group, such as an alkyl group, produces condensation of the C-H bond via a repulsive force. Consequently, Fourier transform infrared (FTIR) spectra of films with organic properties show a blue shift due to compression of the C-H bond. At the equilibrium geometry of a C-H bonding system, the electrostatic attraction between the dipole moments of the proton donor and acceptor must be balanced by the Pauli repulsion. In the absence of orbital interactions, such as electron-withdrawing, this repulsive interaction leads to compression of the C-H bond [15-18].

In this paper, we study on the electrical properties of the fluorinated amorphous carbon films according to the flow rate ratio and annealing effect. The a-C:F film was studied the bonding structure of organic materials from the leakage current by I-V measurements, and the correlation between the dielectric constant and the electrical properties was researched.

2. Experiment

Fluorinated amorphous carbon (a-C:F) film were deposited on a p-type (100) silicon substrate by using an inductively coupled plasma chemical vapor deposition (ICPCVD) with a mixture of carbon tetrafluoride (CF_4) and methane (CH_4) gases for 3 minutes. The wafers were chemically cleaned by a standard cleaning procedure before loading them into the reaction chamber. An inductively coupled plasma (ICP) was generated by means of a four-turn coil, which was set around a quartz tube. The a-C:F films were deposited with various flow rate ratios of CF_4:CH_4. The substrate annealing temperature was varied from 50 ºC to 250 ºC during the I-V measurements. The CF_4 and CH_4 gases were introduced through a mass flow controller (MFC) into the reaction chamber, and the discharge pressure was measured with a Baratron gauge and kept at ~200 mTorr. High density plasma about 10^{12} cm^{-3} was obtained at low pressure with rf power of 800 W, and a base pressure of $\sim 10^{-6}$ Torr was obtained for each experiment. Electrical leakage currents for the films were measured using a metal-insulator-semiconductor (MIS) structure. Al dot area was $750\mu m / 2\times\pi$. The dielectric constant of the films was also obtained by C-V measurements using MIS (Al/a-C:F films/p-Si) structure. Film thickness was measured using a field-emission.

3. Results and Discussion

Chemical shift of a-C:F films by the analysis FTIR and XPS spectra was discussed previous study. a-C:F films displayed the blue and red shifts due to the bonding structures resulting from a function of the flow rate ratio [11].

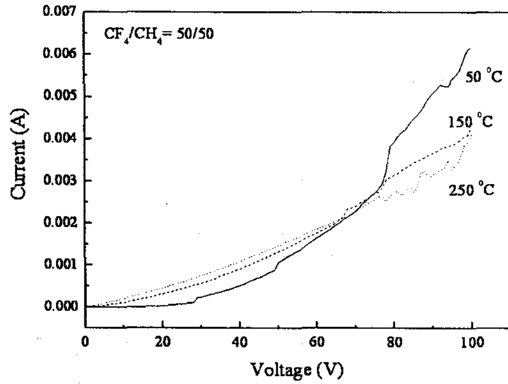

Fig. 1(a) CF_4/CH_4=50/50

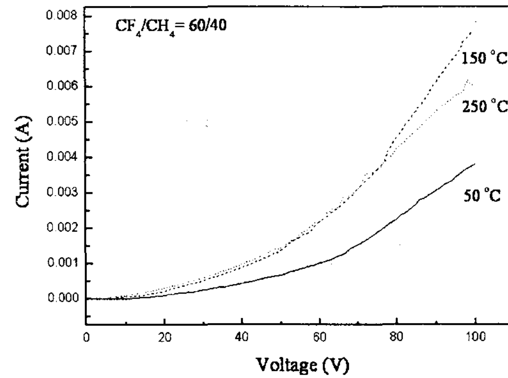

Fig. 1(b) CF_4/CH_4=60/40

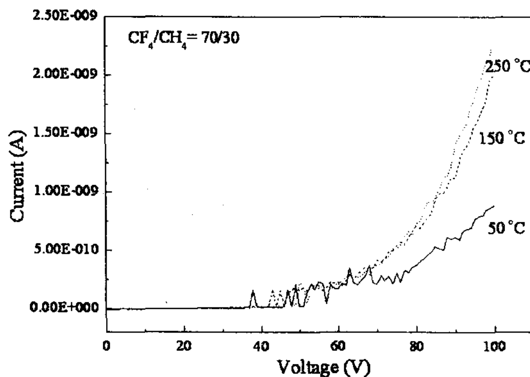

Fig. 1(c) CF_4/CH_4=70/30

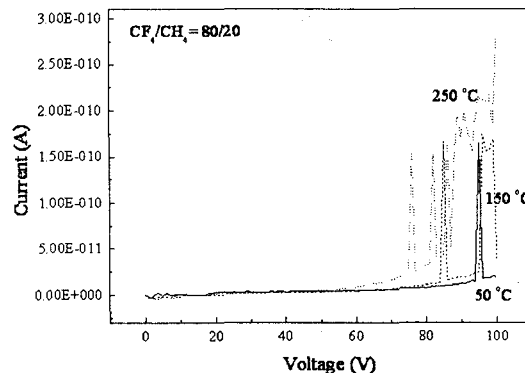

Fig. 1(d) CF_4/CH_4=80/20

Figure 1 shows the leakage current versus the voltage as a function of annealing temperature and the flow rate ratio. The samples of the figure 1(a) and (b) have considerably large leakage current, but the samples of the figure 1(c) and (d) have very small leakage current, notwithstanding small different flow rate ratio. The leakage current increases with increasing the annealing temperature. Generally, the properties as a dielectric materials are good at the samples with increasing the fluorine flow rate ratio.

Figure 2 shows the log current versus the voltage about the same data of Fig. 1, in order to clarify the electrical conduction mechanism. The dielectric persistence is good at the sample as shown in Fig. 2(c), which there is no leakage current in the range from 0 V to near 20 V. The dielectric persistence increases according to the increasing of the CF_4 flow rate ratio.

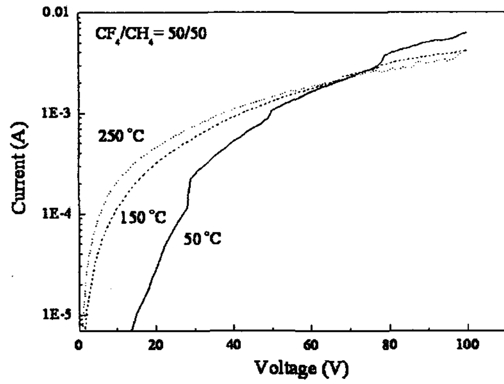

Fig. 2(a) CF_4/CH_4=50/50

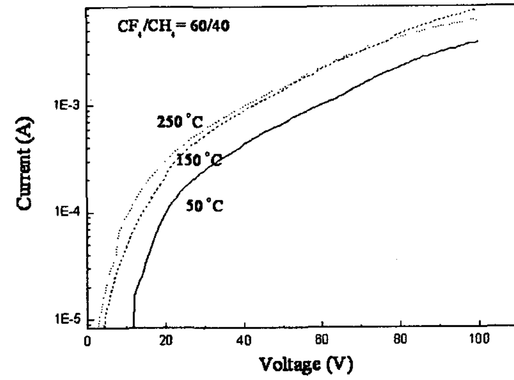

Fig. 2(b) CF_4/CH_4=60/40

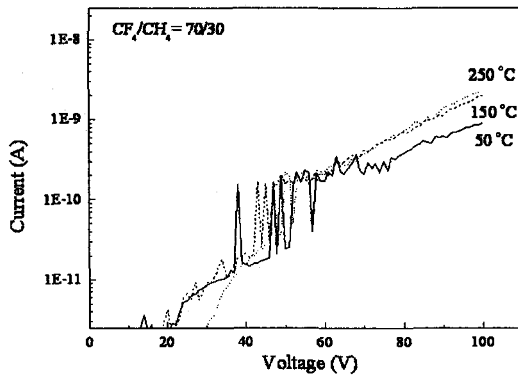

Fig. 2(c) CF_4/CH_4=70/30

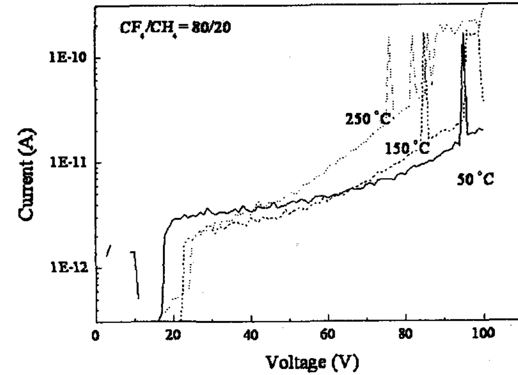

Fig. 2(d) CF_4/CH_4=80/20

Figure 3 shows the dielectric constant of the fluorinated amorphous films as a function of the flow rate ratio. The dielectric constant at the sample of the flow rate ratio with CF_4/CH_4>2.3 does not measured, because the thin films did not deposit due to the high electro-negative fluorine atom. This result is the same as the previous paper except the sample of the flow rate ratio with CF_4/CH_4=4.0 [11]. It is difficult that the results at Fig. 1 and 2 reflect the electrical properties of a-C:F films with the flow rate ratio CF_4/CH_4=4.0. It is said that the elongation of C-H bond due to the fluorine makes voltaic HF bond, therefore, too much fluorine atoms does not contribute to decrease the dielectric constant of the films.

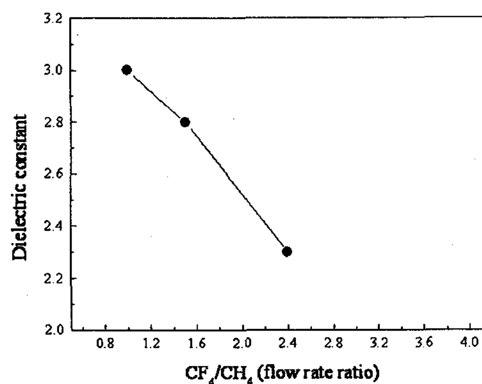

Fig. 3 Dielectric constant of a-C:F films as a function of the flow rate ratio

Figure 4 shows the energy band diagram of a-C:F films after contact in accordance with the bonding structure such as the cross-link amorphous and cross-link breakage structures. Organic materials such as a-C:F films were deposited by the reaction between the C-H bond and neighboring high electronegative atoms. The results reflect the chemical shifts like C-H bond condensation and C-H bond elongation. Physically, the bonding structure of the organic materials is changed by peculiar phenomenon of the C-H bond. a-C:F films with the cross-link breakage structure originates from the C-H bond condensation due to the electro rich attached group. On the other hand, a-C:F films with the cross-link amorphous structure curse the C-H bond elongation due to the electro deficient attached group. These two type of a-C:F films are chemically and physically very different properties. And the electrical properties also show very much difference in spite of very few little difference of the flow rate ratio, as show in Fig. 1 and 2.

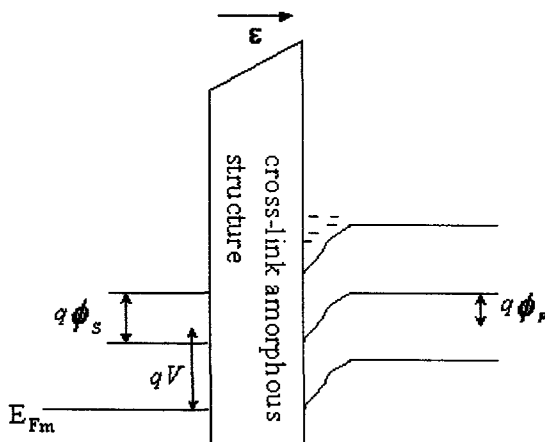

Fig. 4(a) a-C:F film with the cross- link amorphous structure

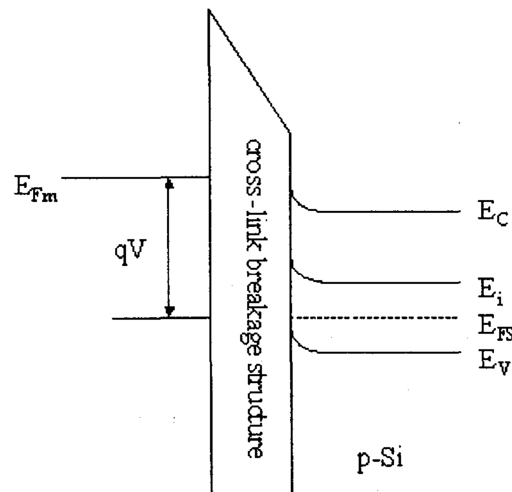

Fig. 4(b) a-C:F film with the cross-link breakage structure

In the case of Fig. 4(a), the high electro-negative fluorine atoms break the C=C double bond and produce the elector deficient group due to the cations. The cations on the Si surface affect to increase the Schottky barrier. Therefore, the leakage current is hard to flow through the MIS structure channel. We could say that the insulator of the cross-link amorphous structure (sample with CF_4/CH_4=2.3) due to the elector deficient group has low dielectric constant because of much fluorine flow rate, and the surface energy distribution on the films by the C-C single bond also improved. On the other hand, the electron rich group affects to decrease the potential barrier and induces the leakage current through the low potential barrier. Consequently, the decreasing of fluorine flow rate causes the electron rich group such as C=C bond, and increases the dielectric constant in the insulator of samples with $CF_4/CH_4 \leq 1.5$ as shown in Fig. 4(a). It is said

that the peculiar phenomenon of C-H bond is useful chemical interactions to present not only low dielectric constant but also good adhesion in organic compound as low-k materials

4. Conclusions

The electric properties of a-C:F films are divided into two types according to the bonding structure such as the cross-link breakage and cross-link amorphous structures. a-C:F films with the cross-link amorphous structure has the lowest dielectric constant and the electric properties with very small leakage current. These results originate from the C-H bond elongation due to the electro deficient group. We confirmed that the peculiar phenomenon of C-H bond in organic materials could also improve the electrical properties by the control of the potential barrier in surface of the films.

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