Characterization of polymer-like thin films deposited on silicon and glass substrates using PECVD method


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Abstract

Polymer-like thin films have been deposited on glass and silicon substrates at temperatures in the range 300–673 K, by a plasma enhanced chemical vapor deposition (PECVD) method using thiophene (C₄H₄S) as a precursor. A power with radio frequency (13.56 MHz) was applied for the ignition of the plasma, and hydrogen and Ar (argon) were used as the bubbler and the carrier gases, respectively. In order to compare physical properties of the as-grown thin films, an effect of the plasma power and deposition temperature on the dielectric constant and thermal stability were mainly studied. XRD and FT-IR studies revealed that the as-grown films at 373 K have highly oriented amorphous polymer structure. XPS revealed that the polymerized thin films have the same stoichiometric ratio (8:1) between C and S, indicating that dimer-like thin films were mainly grown under our experimental condition. From the electrical properties measurements such as I–V and C–V characteristics, we knew that the relative dielectric constants increased from 2.96 to 4.0 when the RF power was increased up to 200 W. Moreover, the leakage current density was increased with increasing RF power and deposition temperature. The maximum deposition rate obtained was 110 nm/min for the polymerized thin film deposited at 300 K and 100 W. The activation energy for polymer-like thin film deposition calculated from the Arrhenius plot was ~6.9 kJ/mol, signifying that a diffusion control process was the rate-determining mechanism.

Keywords: Polymer-like thin film; PECVD; Thiophene precursor; Low dielectric constant; Leakage current density

1. Introduction

There has been an increase of interest in the use of glow discharge for the polymerization of a number of organic and organometallic compounds. Plasma polymers are used as dielectric and optical coating to inhibit corrosion [1,2]. The investigation of the optical properties of polymer films is in particular interest because of their use in optical devices [1]. Moreover, with the increasing integration density of semiconductor devices, multilevel metallization technology is even more important than it used to be [3]. In advanced logic devices with quarter micron design rules, the number of interlayer dielectrics has increased to four or five times, so that wiring delays are beginning to dominate the total signal delay in ultra large scale integrated circuits (ULSI). To lower the propagation delay, the most important issue will be how to lower the dielectric constants ($k \leq 3.0$) of interlayer dielectrics rather than lowering the resistance of interconnect metals [3,4]. High thermal stability ($\geq 723 K$) as well as low dielectric constants are also important requirements for the interlayer dielectrics.

Studies of thiophene oligomers are driven by potential applications in nonlinear optical and electroluminescent devices, and in semiconductor-based components. Over the last years, there is a growing interest in organic polymer thin films, which can applied in many fields of electrical or electronic engineering, for example, as light-emitting diodes (LEDs) or thin film transistors (TFTs) or insulating materials [5]. Among many CVD methods plasma enhanced chemical vapor deposition (PECVD) process is very efficient method to produce homogeneous organic thin films on large area substrates and offers good control over the film properties [6–10]. PECVD can also deposit thin films of polymers with an organic
precursor without halogen species, which can be incorporated into the film during the deposition and destructed the contact materials such as metals. Moreover, plasma polymerized films that can be deposited very conveniently and reproducibly with high optical quality, adherent, and pinhole-free properties.

In this study, we reported here our primarily results of the growth of polymer-like thin films on glass and silicon substrates in the deposition temperature range of 300–673 K using the thiophene precursor by PECVD method for low dielectric and optical devices applications. In addition, an effect of deposition temperature and plasma power on the dielectric constants and deposition rate were mainly described. Our objectives are to obtain the polymer-like thin films with low dielectric constant of below 3.0, high thermal stability of even 673 K, low leakage current density of below $10^{-8}$ A/cm$^2$ at 1 MV/cm, and high optical properties.

2. Experimental

The experiment was carried out in a home-made vacuum chamber which is consists of stainless steel. The glass and silicon have been used as substrates that cleaned and etched using acetone, isopropyl alcohol, HF(48%-Si wafer) solution, and DI(distilled) water, sequentially. After cleaning the samples, the pre-cleaned substrates were in situ pre-treated with Ar plasma to make an oxygen-free surface and a buffer layer for enhance film adhesion, respectively. The deposition was lasted for 2–20 min, depending on the RF power and deposition temperature. The general deposition pressure and temperature were 2–4$\times$10$^{-1}$ Torr and 300–673 K. The substrates were heated using indirect heating method and the temperature of the chamber wall was detected by Chromel–Alumel thermocouple. The typical conditions of PECVD process applied in this study for film deposition are 30–200 W of RF power and 20 sccm of Ar carrier gas, and 20 sccm of H$_2$ bubbler gas. Thiophene (C$_4$H$_4$S) was used as organic precursor. Due to high vapor pressure of the precursor itself, it was not necessary to heat the source during deposition. The as-grown plasma polymer-like thin films were ex situ characterized with X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), FT-IR, UV–vis spectroscopy, and scanning electron microscopy (SEM).

Impedance analyzer was utilized for the determination of $I$–$V$ curve for leakage current density and $C$–$V$ curve for dielectric constants, respectively. The dielectric constants of the as-grown films were calculated from capacitance data measured at 1 MHz. To measure the electrical properties of the as-grown films, Al as the electrode was evaporated on the thiophene films that grew on Pt coated silicon substrates, and the $I$–$V$ and $C$–$V$ curve of each MIM (metal-insulator-metal) structures were then measured.

3. Results and discussion

The resulting films were in first analyzed with X-ray diffractometry. Fig. 1a shows the typical X-ray diffraction pattern of a plasma polymerized thin film grown on Si(100) substrate with thiophene precursor at 373 K and 200 W. XRD pattern of Fig. 1a showed a hint of highly oriented amorphous film formation. At $2\theta=5–25^\circ$, the two peaks with large intensity and broad peak width gave the information of an existence of some crystallized amorphous structure. From the previous literature [11,12], the same XRD peaks as our data have been observed from a bulk thiophene polymer that obtained under a solution phase.

Fig. 1b shows FT-IR spectra of thiophene monomer and as-grown thin films. Based on the FT-IR data obtained from the polymerized thiophene [8] and toluene [7] films by PECVD, we analyzed our IR data as following. The absorption peak at 2910 cm$^{-1}$ can be assigned to the aliphatic C–H stretching mode by methyl and/or methylene groups. The threefold C–C bond of a fragment from the thiophene ring can be found at 2200 cm$^{-1}$. This shows that a considerable amount of monomer fragmentation takes place during the plasma polymerization. Thus, the plasma polymerized thin films with thiophene precursor can exist as a mixture of dimer, trimer, etc. The C=C structure may also be originated from the mesh structure of the thin film, which is usually observed in the plasma polymerized films [9]. In addition, we could see the increase of absorption peak intensities whenever the polymerization was carried out at high RF power. This indicates that more high quality films can deposited using high RF power. Thus, we obtained a crystallized polymer thin film with amorphous structure under the condition of 200 W RF power (see Fig. 1a).

Fig. 1c,d show UV–vis absorption (Fig. 1c) and transmittance (Fig. 1d) spectra of the plasma polymerized thin films that grew on glass substrates at 373 K under the condition of Ar:H$_2$=1:1 and different RF powers. In the Fig. 1c, we can see that the maximum absorption peaks which was contributed to $\pi–\pi^*$ transition was observed at approximately 316–328 nm and shifted to long wavelength with increasing RF power. The width of absorption band was also increased with increasing the RF power. Appearing a red shift and wider peak width with RF power reflects a formation of high cross-linking density and $\pi$-electron conjugation bond in the polymer-like thin films. It may thus appear that with increasing RF power, high degree cross-linking density of the $\pi$-electrons could be overlapped, resulting in formation of more stable polymers. The increase of absorption peak intensity with increasing the RF power can be explained with either the increase of carbon contents or the scattered reflection caused by plasma bombardment. Higher transmittance than 90% could be
obtained from the most of polymerized films grown at 300 K and RF powers of below 200 W (see Fig. 1d). However, the optical transmittance was decreased with increasing RF powers due to high amount of carbon in the film layers. We confirm the increase of carbon amount with increasing the RF power by XPS data, and compare our data with reported results previously [1]. Fig. 1d also shows the changes of optical transmittances and gave a band gap shift to the higher wavelength with RF powers. With the straight-line interception at near band-edge of 316–328 nm where the transmittance drops sharply off to zero, we can calculate an indirect band gap of the polymerized thin films. The obtained band gap was varied from 3.79 to 3.93 eV with increasing RF powers, suggesting an acceptable insulating property.

Fig. 2 shows the X-ray photoelectron survey and high resolution spectra obtained before and after Ar ion sputtering for a polymerized film grown on Si(100) at 373 K and RF power of 100 W. The survey spectrum (Fig. 2a) clearly shows the photoelectron peaks of S 2s, S 2p, and C 1s and C (KVV) Auger signal as well as O 1s and O (KVV) Auger transition. After Ar$^+$ ion sputtering for 1 min or even more (see Fig. 2b), however, we did not detect any oxygen species through the film layers, signifying the formation of oxygen free polymerized thin film. This indicates that the oxygen layer exist only in the surface region of the thin films because of no oxygen contamination of the newly formed film by air and/or moisture during sample transfer. In the Fig. 2c,d the high resolution XP spectra of C 1s and S 2p were also shown. The main features of these spectra initially appeared at approximately 287 eV (C 1s) and 171 or 166 eV (S 2p), respectively. The reason for arising at two S 2p peaks is attributed to the existence of two different species, i.e. SO$_x$ (171 eV) and thiophene polymer (166 eV). However, the peak due to SO$_x$ species disappeared after sputtering. Moreover, we can see that due to a charging effect both the major peaks of C 1s and S 2p are shifted to lower binding energy by 3 eV and appeared with the same intensities, suggesting a polymer-like thin film formation with the same stoichiometry between carbon and sulfur at various RF powers. The composition ratio of carbon and sulfur in the film was obtained to be approximately 8:1. This indicates that the as-grown films can exist with a majority of dimer form and/or mixture of monomer+trimer. Precisely speaking, the carbon con-
Fig. 2. XPS survey spectra obtained before (a) and after (b) sputtering for a polymerized film that grown at 373 K and RF power of 100 W. Figures (c) and (d) show the high resolution XPS data of (c) C 1s and (d) S 2p obtained from the same sample before and after sputtering.

tents were increased from 86.7 to 88.6% with increasing the RF power from 50 to 100 W, while those of sulfur were decreased from 13.3 to 11.4%. This means that the carbon remains constantly through the thin films, while some of the sulfur could be desorbed due to the influence of Ar+ ion bombardment that ignited by high RF power. By the comparison of these XPS data with UV–vis spectra, we can confirm that the carbon makes an important role of depending on the extents of band gap and on the transparent property of thin films.

Fig. 3 shows surface morphologies and cross-sectional SEM image of the as-grown films obtained at various condition of RF powers and 373 K. Fig. 3a, b and c, obtained for the polymerized films grown on Si(100) substrates at RF power of 50 W (Fig. 3a), 70 W (Fig. 3b), and 100 W (Fig. 3c), respectively, show smoother and featureless surfaces with increasing the RF power. We obtained the most smooth film under the RF power condition of 100 W. This result can be explained by a difference of plasma density because the more high plasma power can easily break monomer and cluster in the gas phase or on the surface. In the cross-sectional SEM image (Fig. 3d), we recognized that a 3-μm thick film with very sharp interface between the thiophene film and silicon substrate was obtained in the condition of RF power 200 W, Ar:H2 = 1:1. The sharp interface suggests a good adhesion and a homogeneous film in the depth.

The film growth rate were determined as a function of RF power and deposition temperature in the range of 30 W–100 W and 300 K–673 K, respectively. Fig. 4a shows the maximum growth rate (110 nm/min) when the film was grown at 300 K and 100 W of RF power. This is a quite higher value compared with that grown by the conventional method. When the plasma power was increased, the deposition rate was increased at room temperature (see Fig. 4a). The increase of the deposition rate with increasing RF power can be simply explained in terms of the increase of plasma density with enough available energy which can be used for plasma polymerization of thiophene precursor. In the condition of 373 K, the deposition rate was also increased very slowly with increasing the RF power from 30 to 50 W. Above 50 W, however, the deposition rate was decreased with increasing RF power up to 100 W. Therefore, the deposition rate shows a strong dependence on the deposition temperature. To identify this tendency more clearly, we deposited the polymerized thin films at various deposition temperatures under the same RF power of 30 W, deposition pressure and gas flux. Fig. 4b shows the variation of deposition rate as a function of growth temperature. The figure shows a maximum
point at 393 K and then decreased rapidly with increasing deposition temperature. Noticeable thing is that the film can deposit at even 693 K, suggesting that our as-grown thin film at 693 K have good thermal stability at high temperature. Fig. 4c shows the Arrhenius plot obtained from the Fig. 4b. Using least square method, an activation energy of plasma polymer-like thin film deposition was obtained to be $-6.9 \text{ kJ/mol}$ from the slope of the Fig. 4c, suggesting that our polymerization process was mainly governed by a diffusion rate control. The mean of slight negative value indicates that desorption and/or pre-adsorption process have also occurred during CVD. Below 393 K, however, positive activation energy (1.3 kJ/mol) was also obtained. Similar results have been observed in the previous paper [2] that obtained the $E_a$ as 0.95 kJ/mol for xylene polymerized film and 2.21 kJ/mol for toluene polymerized film, respectively. This means that surface reaction will also be one of the main processes for the film deposition mechanism.

Fig. 5a shows a change of dielectric constants obtained using impedance analyzer (at 1 MHz) from the thin films grown on Si(100) substrates at various RF powers, 373 K, and Ar:H$_2$ = 1:1. In the condition of 50 W, we could get the lowest dielectric constant to be $k = 2.96$. The insulating properties of plasma polymerized thin films grown on Si(100) substrates at 373 K and RF power from 50 to 100 W were also investigated by measuring the leakage current density $J$ with different applied field $F$, which is shown in the Fig. 5b as a function of RF power. As the plasma power increases from 50 to 100 W, the leakage current densities were increased very slowly and the breakdown did not appear below 2 MV. This indicates that our films have a compact structure with high density and pin-hole free layers that are well known to have a lower leakage current density and higher breakdown field. Therefore, our plasma polymerized organic films were almost conjugated and have high cross-linking density. The leakage current density of a thin film grown at 373 K and below 70 W of RF power is shown below $10^{-9}$ A/cm$^2$ at 1 MV/cm suggesting that this polymer thin film can be applied in the insulating material to the semiconductor devices as DRAM.

4. Conclusions

Polymer-like organic thin films were deposited at temperature in the range of 300–673 K by PECVD method using the thiophene (C$_6$H$_5$S) precursor. Oxygen
free polymer films with smooth surface and optically transparent could be grown on various substrates. We compared to the deposition rate (nm/min) of thin films as a function of deposition temperature and RF power in the range of 30–100 W. The lowest dielectric constant \( k \) was 2.96 for a thin film grown at 373 K and RF power of 50 W, and the highest deposition rate was approximately 110 (nm/min) at 300 K and RF power of 100 W, respectively. In the condition of Ar:H\(_2\)=1:1, RF power of 50 W and 300 K, moreover, the best leakage current density was obtained to be below \( 10^{-10} \) A/cm\(^2\) at applied field of 1 MV/cm.

Fig. 5. Changes of electrical properties as a function of RF powers; (a) dielectric constants and (b) leakage current density.

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