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AFM and XPS Study on the Surface and Interface States of CuPc and SiO_2 Films

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Abstract: A CuPc/SiO_2 sample is fabricated. Its morphology is characterized by atomic force microscopy, and the electron states are investigated by X-ray photoelectron spectroscopy. In order to investigate these spectra in detail, all of these spectra are normalized to the height of the most intense peak, and each component is fitted with a single Gaussian function. Analysis shows that the O element has great bearing on the electron states and that SiO_2 layers produced by spurting technology are better than those produced by oxidation technology.

Key words: CuPc/SiO_2; X-ray photoelectron spectroscopy; surface and interface analysis
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1 Introduction

Organic field-effect transistors (OFETs) have attracted tremendous attention due to their potential applications in low-end electronics[1~5]. Exciting advances have been made recently as a result of the adoption of new organic materials[6,7], more advanced film formation technologies[8,9], and the surface modification of electrodes[10]. Although the interaction of insulators with semiconductors is seldom characterized and demonstrated, it is very important for OFETs. Veres *et al.*[11] illustrated that this interaction can greatly change the density of states (DOS) of a semiconductor layer near an insulator layer, resulting in a lower operating voltage and higher field effect mobility μ_{FET}.

In addition, CuPc and SiO_2 have been widely used in OFETs, and good performance has been achieved with them[12]. In view of the important role of the interaction between insulators and semiconductors, the study of the surface and interface states of CuPc/SiO_2 is significant. That is the focus of this work, the aim of which is to improve the performance of OFETs based on SiO_2 and CuPc and to understand mechanisms of degradation in OFETs.

2 Experiment

Polished Si wafer was used as a substrate. Prior to producing the SiO_2 layer, the wafer was carefully rinsed to remove the contaminants. Then at 1150 ℃, it was loaded into an oxidation oven to produce the SiO_2 layer first by wet oxygen for 30min, and then immediately thereafter by dry oxygen for 15min. Finally, a 230nm thick SiO_2 layer was obtained, which was then immediately transferred into the deposition chamber to form a 50nm thick active layer (CuPc) by thermal evaporation technology. The CuPc (Fig. 1) powder was purchased from Aldrich Chemical Co. and was purified by sublimation technology several times before it was used. The distance from the substrate to the source was 15cm, the substrate's temperature was 210 ℃, the background pressure was 4.13×10^{-4} Pa, and the deposition rate was 0.4nm/s.

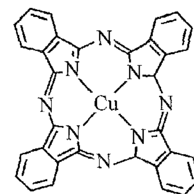

Fig. 1 Chemical structure of CuPc molecule

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The morphology of the CuPc surface on the SiO_2 layer was characterized by high-resolution AFM. The electron states of the surface and interface of CuPc/ SiO_2 were investigated by VG MKII X-ray photoelectron spectroscopy. Al Kα radiation ($h\nu$ = 1253.6keV) was used as the X-ray source and was operated at 300W. The sample was sputtered by an argon ion beam with a kinetic energy of 2.0keV at 2×10^{-7} Pa argon pressure. In order to avoid the selective sputtering effect, which could damage the surface of the CuPc/ SiO_2 sample and the CuPc molecular structure, a large area (1.5cm × 1.5cm) and low energy (1.0μA) were used. The scanning energy region ranged from 0 to 1050eV, and the scanning step was 50meV.

3 Results and discussion

Figure 2 shows the morphology of the CuPc thin film deposited on the SiO_2 layer. It is evident that the CuPc thin film produced was of good quality, with a surface roughness of less than 15nm. Nevertheless, there are many islands in it, connected with each other in random directions, with the result that the surface is a little amorphous and has many holes distributed in it, which may result from the Stranski-Krastanov growth mode[13] of thermally evaporated CuPc film.

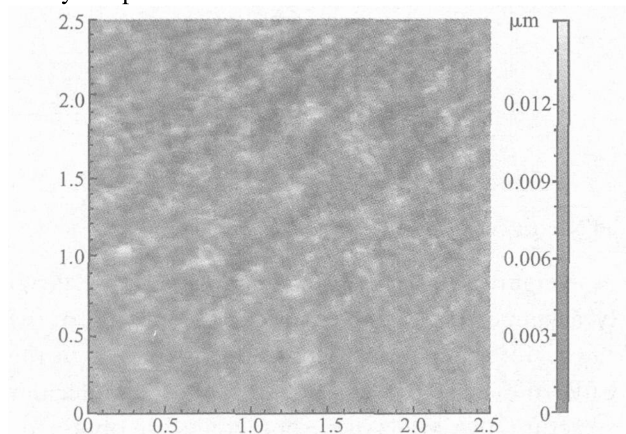

Fig. 2 AFM images of the morphology of the surface of CuPc/ SiO_2 sample

The electron states of the surface and interface of the CuPc/ SiO_2 were investigated by XPS. In order to isolate the sample from O_2 atmosphere, it was kept in an N_2 environment before it was characterized. In addition, in order to remove the O_2 molecules absorbed at the CuPc film surface, the first XPS spectrum was measured after it was sputtered for 2min. Other spectra were acquired at the 5, 8, 11, and 14th minutes.

Figure 3 shows the whole scanning spectrum of the CuPc surface at the 2nd minute. There are strong peaks at 283, 397, 532, 933, and 953eV, which correspond to the C1s, N1s, O1s, and Cu2p electron states. Here, neither a Si atom nor a B atom signal appears in this spectrum, suggesting that the CuPc layer is thick enough to cover these atoms completely. The Cu2p, O1s, N1s, and C1s fine spectra are shown in Fig. 4. In order to investigate the electron states in detail, all of them have been normalized to the most intense peak, and each component has been fitted to a single Gaussian function. Moreover, the area evolution of each element with the sputtering time (t_s) is recorded in Fig. 5.

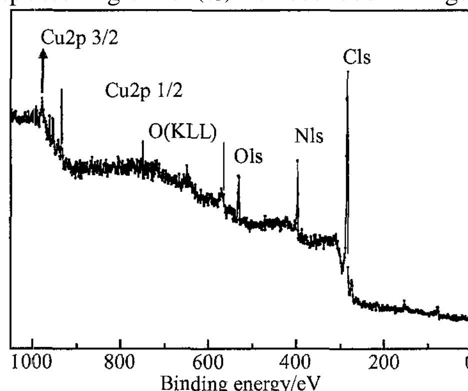

Fig. 3 XPS whole-scanning spectra recorded at the pristine surface of the CuPc/ SiO_2 sample

Figure 4 (a) illustrates the fine spectrum of the Cu elements. At 2 minutes, there were two strong peaks located at 954.05 and 934.09eV, attributed to the Cu2p 1/2 and Cu2p 3/2 states, respectively[14]. The Cu2p 1/2 state (bonding energy of 954.05eV) indicates that the copper in the CuPc molecule is in the Cu (Ⅱ) state, which can be further confirmed by the chemical structure of the CuPc molecule (Fig. 1). Several satellite peaks of Cu (Ⅱ) are also observed, which come from the influence of the $3dx^2 - y^2$ orbital that is derived from the flatness of the CuPc molecule.

Figure 4(b) shows the fine spectrum of O1s. In fact, there is no oxygen in CuPc. The oxygen can only result from the diffusion of O in the SiO_2 layer (source A) and of H_2O and O_2 molecules absorbed at the CuPc film surface (source B). Here, we think the oxygen at 2min mainly originated from

source B ,which is also apparent from the fact that the oxygen content first decreased (before 2min) , then nearly keep constant (2～5min) ,and finally increased (after 5min) with t_s (Fig. 5) . According to the diffusion rule ,it is evident that before 2min , in the 2～5min range ,and after 5min ,the oxygen mainly came from source B , sources A and B ,and source A ,respectively. Furthermore ,Figure 4(b) is not so regular ,and the peak is wide (about 2eV) , because there are seve-ral O-containing materials in the CuPc layer (e. g. ,O_2 ,H_2O ,and O ions) and all of them interact with CuPc molecules. Figure 4(b) also shows that with the increase of t_s ,the shape of the O1s fine spectrum gradually becomes more regular ,indicating that one of the materials (O_2 ,H_2O , or O ion) diffused from SiO_2 layer has become dominant.

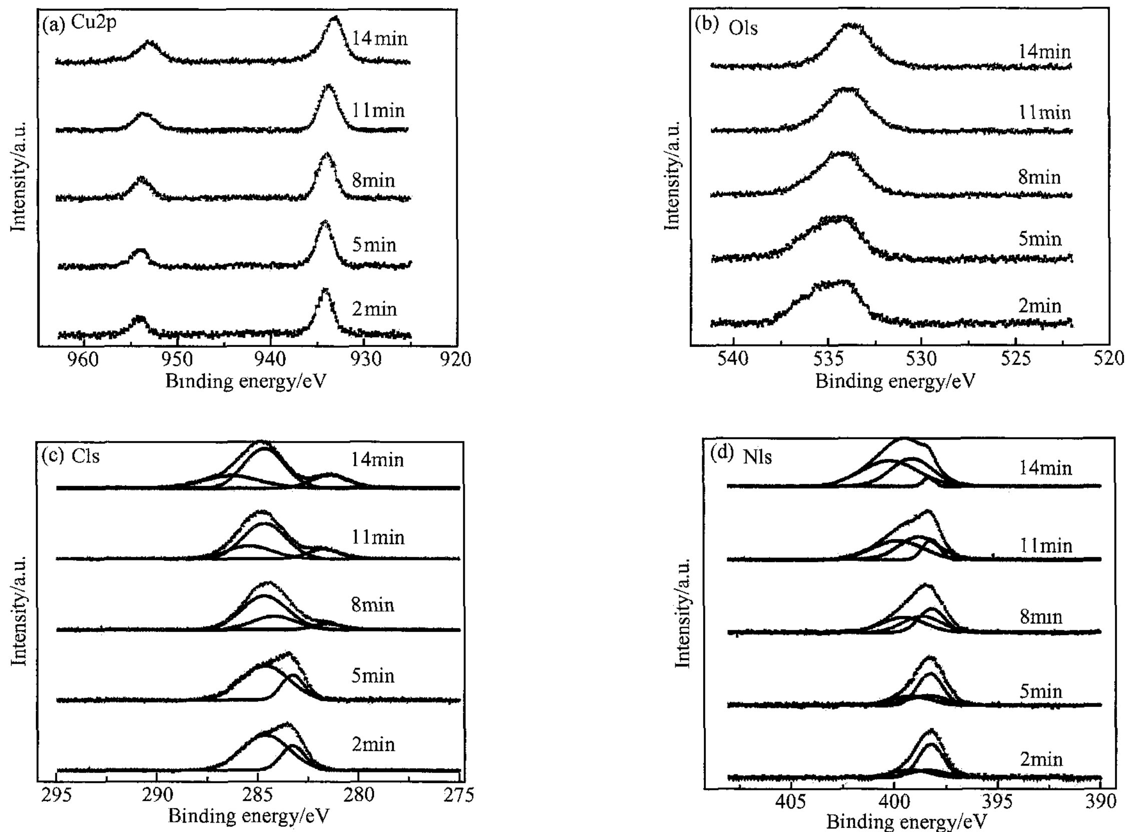

Fig. 4 Evolution of Cu2p (a) ,O1s (b) ,C1s (C) ,and N1s (d) core level peaks as functions of t_s

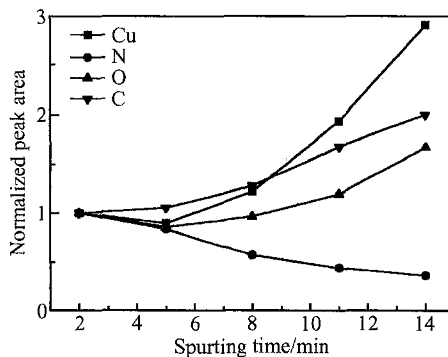

Fig. 5 Evolution of the normalized peak area of as functions of t_s

Figure 4(c) is the spectrum of C1s. It is clearly asymmetrical ,which can be accounted for by the different chemical environment for C1s in the CuPc molecule. By analyzing CuPc 's molecular structure ,two kinds of carbon bonds are obtained. The first is the C - C = C bond ,derived from the aromatic carbon atoms which interact with hydrogen (H) or other carbon (C) atoms in the aromatic rings. There are a total of 24 in one CuPc molecular. The other is an N - C = N bond ,in which the C atom not only interacts with one aromatic C atom , but also with two nitrogen (N) atoms. There are 8 of these in one CuPc molecule. Furthermore ,by fitting to a Gaussian function ,two symmetrical spectra (Fig. 4(c)) with peaks at 284. 64 and 283. 24eV

are obtained.

It is well known that the binding energy of an element is related to the electronegativity of the atom bonding with it. The larger the electronegativity of the related atom, the smaller the electron density is around the C atom. Taking into account that the electronegativity of C and H atoms are less than that of an N atom, the binding energies of 283.24 and 284.64eV can be ascribed to the C - C = C and N - C = N bonds, respectively. According to the Gaussian fit, the peak area ratio between the 284.64 and 283.24eV peaks was nearly 3 ∶1 (22012 ∶7689.9), agreeing well with the analyzed results (24 ∶8) for C atoms in a CuPc molecule. Thus the bonding energy of 283.24eV actually results from the N - C = N bond, and 284.64eV is from the C - C = C bond. This also has been shown in other literature[15~17]. It is believed that this is because the electronegativity of the N atoms was decreased because N atoms not only interact with C atoms but also with the central metal (Cu) atom.

As for N1s, the fine spectrum is shown in Fig. 4(d). Due to the interaction with different atoms (Fig. 1), namely, four N atoms with two C atoms and the other four with C and Cu atoms, it is similar to C1s: two components in the fine spectrum of C1s are anticipated. At first glance, the N1s spectrum (Fig. 4 (d)) at 2min seems approximately symmetrical and roughly fits a Gaussian function. This is because the sample was saved in N_2 atmosphere before it was sent to the XPS analyzer. Thus many N_2 molecules were absorbed at the surface and further diffused into the CuPc layer, ultimately shielding the N signal of the CuPc molecule. This deduction is reasonable and was confirmed by further investigation when the sample was continuously sputtered, removing most of the absorbed N_2 molecules. Other fine spectra (at 5, 8, 11, 14min) were then recorded, of which all the relevant peaks are shown. By means of fitting to a Gaussian function, two peaks of approximately equal area centered at 397.73 and 398.52eV were marked when t_s reached 5min. The peak at 398.52eV results from the N atom that interacts with two C atoms[18], while the other at 397.73eV is from the N atom bonded with both C and Cu.

To further understand the electron states of CuPc/SiO_2, the evolution of C1s, N1s, O1s and Cu2p as functions of t_s is illustrated in Figs. 4(a)～(d). Note that when t_s is between 2 and 5min, the N content changes greatly, while O remains nearly constant. This may be due to the comparable diffusion ability of O between source A and source B in this range.

When t_s increases from 5 to 14min, Figure 4 shows that the C1s and Cu2p content increases too. Surprisingly, it is not a constant. Here, we derived it from the Stranski-Krastanov growth mode of CuPc film, which resulted in a higher density of CuPc molecules at the bottom (compact) than on the top (incompact). This conclusion agrees well with the AFM results mentioned above. The increase of Cu content may also result from another aspect, in which the Cu atoms detach themselves from CuPc molecules at the surface and diffuse into the CuPc layer[19]. At the same time, the N content declines, while the O content increases to some extent. The former is because of the decrease of N_2 concentration along the depth, while the latter is because of the continuously strengthened diffusion ability of O from the SiO_2 layer as the interface was gradually approached.

Here, note that O in this range is different from that at 2min. There are two main reasons for this. The first are the O ions. They previously interacted with Si atoms, and later some of them diffused into the CuPc layer, which is also evident by the strong interaction of Si atoms with C atoms, which we will analyze later. The other reason is the redundant H_2O and O_2 molecules that were stored in the SiO_2 layer that did not react with Si in the oxidation process. In view of this, it is certain that the SiO_2 layer produced by sputtering technology is better than that produced by oxidation technology. When t_s further increased to exceed 14min, the N1s and Cu2p content began to decrease. Meanwhile, the Si2s and O1s signals increased strongly, implying that the interface of CuPc/SiO_2 had been excited.

Besides these, different chemical shifts of C1s, O1s, N1s and Cu2p were also observed when the interface of CuPc/SiO_2 was approached. At the beginning (t_s was at 2～5min), the peaks of C1s, O1s, and N1s were almost stable, with no obvious alternation (Fig. 4). When t_s increased, the changes in these spectra appeared, reflecting the interaction of the insulating layer (SiO_2) with the active layer

(CuPc). In order to accurately analyze the XPS results, the spectra of N1s, C1s at 2, 5, 8, 11 and 14min all were fitted to Gaussian functions, respectively.

We first consider the N1s spectrum. By virtue of the Gaussian fit, Figure 4(d) shows three components included in the N1s spectrum. The two spectra of approximately equal area are ascribed to the N atoms of the CuPc molecule and are located at 397.73 and 398.53eV at 2min, and the other originated from the N_2 molecules diffused from CuPc film surface and is at 397.62eV. As t_s increased, it was evident that the overall peak area of N was also continuously decreasing, mainly resulting from the decrease in N_2 concentration (the third peak). In addition, the shape of the N1s fine spectrum slowly broadened, suggesting that N atoms in the CuPc molecules strongly interact with O diffused from the SiO_2 layer. Furthermore, Figure 4 (d) shows that near the interface (at 14min), the peaks shifted by about 0.8eV to a higher bonding energy, which was derived from the interaction with O.

As for the O, the area of O1s continuously increased with t_s because of the gradual approach to the CuPc/ SiO_2 interface. In addition, the most conspicuous characteristic of the O1s spectrum is the width of the peak (1～2eV). This is because several components (e.g., H_2O, O_2 and O ion, which were been mentioned above) were included, and all of them interact with other atoms in the CuPc molecule. Due to interaction with other elements and its function as an electronegative atom, the peak of O moved to a lower bonding energy (about 0.9eV at 14min).

Figure 4(a) displays two separate spectra. As analyzed above, they correspond to the electron states of Cu2p 1/2 and 3/2. When t_s increases, the areas of the two spectra both increase since the film was produced by the Stranski-Krastanov growth mode. Besides this, the Cu2p 1/2 and Cu2p 3/2 electron states also underwent shifts of 0.99 and 0.82eV to lower binding energies. They changed from 954.04 and 934.09eV at 2min to 953.05 and 933.27eV, at 14min, respectively.

Taking into account that the Cu atoms only bond with N atoms, the interaction of Cu-N is weaker at the interface than that at the surface. This result accords with the analysis of N1s, in which N atoms interacted with O atoms, resulting in the lower electronegativity of the N atoms. Thus the binding energy with Cu atoms decreased.

As for C, the spectrum includes two components whose peaks are located at 284.64 and 283.24eV when t_s is 2min. As t_s increases, both of them underwent a negative chemical shift, indicating a peculiar interaction between the C and N atoms. When t_s reaches 14min, as can be seen from the Gaussian fits, three components with peaks at 281.33, 284.64, and 286.24eV were obtained. It is interesting that a new component whose peak was distinctly marked at 281.33eV appeared, which was greatly separated from the C-C=C and N-C=N bonds. By integrating the spectra, the corresponding areas of $A_1 = 10323$ (281.33eV), $A_2 = 33960$ (284.64eV), and $A_3 = 15365$ (286.24eV) were obtained. The area ratio $[(A_1 + A_2) : A_3]$ is nearly 3 : 1, indicating that the peak at 281.33eV originated from the C atoms of the aromatic rings. Undoubtedly, such a large negative chemical shift could only result from the very strong interaction of C atoms with other atoms, i.e., the Si and boron atoms diffused from the SiO_2 layer. By further comparing with the Si-C bond[20], we find that the interaction is between C and Boron, because Boron is more electropositive than Si. Here, this deduction further supports the conclusion that for OFETs, SiO_2 layers produced by sputtering technology are more advantageous than those produced by thermal oxidation. Furthermore, Figure 4 (c) also shows that the binding energy of other C atoms of aromatic rings [C-C=C] remained nearly constant, while the C binding energy of N-C=N moved from 283.23eV at 2min to 286.24eV at 14min. This shift is large, and it is believed to result from the strong interaction of C atoms with the O that diffused from the SiO_2 layer, which can acutely decrease the binding energy of C atoms[20].

4 Conclusion

In summary, a CuPc/ SiO_2 sample was fabricated in this work. AFM and XPS were used to study the surface and interface states, respectively. Results show that the binding energy of C with N in the CuPc molecule is less than that between C and C atoms. The O atoms diffused from the SiO_2 layer have great bearing on the CuPc molecule, causing N1s, C1s, O1s and Cu2p to undergo different chem-

ical shifts. For example, N1s underwent a positive shift, resulting in a weaker interaction with the Cu and C atoms, and the Cu2p was degraded by about 0.9eV. Moreover, about one third of the C atoms of aromatic rings of the CuPc molecule were found to strongly interact with boron atoms near the interface, making a new component appear in the C1s spectrum, and resulting in a great chemical shift of C1s. All these show that for OFETs, SiO_2 produced by sputtering technology is more advantageous than that by thermal oxidation.

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$CuPc/SiO_2$ 表面界面的电子状态研究

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摘要: 利用热生长工艺和热蒸发方法分别获得 CuPc 和 SiO_2 薄膜层,通过原子力显微镜和 X 射线光电子能谱对其表面界面电子状态进行了研究,并采用高斯拟合方法对各谱进行了详细分析. 结果表明,在氧原子的作用下,N1s, C1s, O1s 和 Cu2p 都经受了一定的化学位移,从而使得各原子间的相互作用强度有所改变,这是导致 OFET 性能劣化的重要原因之一. 对 OFET 而言,采用溅射工艺制备的 SiO_2 层应比热氧化生长的 SiO_2 层更合适.

关键词: $CuPc/SiO_2$; X 射线光电子能谱; 表面界面分析

PACC: 2930K; 7100; 7340

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