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# Twin-layer films of copper phthalocyanine and amorphous titanyl or vanadyl phthalocyanine

## an x-ray photoelectron spectroscopic study

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Metallophthalocyanine (MPc) twin-layer thin films on glass substrates, consisting of copper phthalocyanine (CuPc) overlayer and amorphous vanadyl phthalocyanine (VOPc) as well as titanyl phthalocyanine (TiOPc) buffers, were found to have different gas sensing characteristics. These twin-layer thin films were studied using x-ray photoemission spectroscopy. Photoelectrons of either V or Ti core levels were found to be present at the surface, indicating the existence of possible molecular migrations. The stability of the twin-layers under thermal annealing up to a maximum temperature of 250°C and low-energy Ar ion bombardment was also examined and compared with that of CuPc directly grown on the substrates. We concluded that the twin-layer structures were thermally fairly stable. Ar ion bombardment, however, caused substantial damage to the Pc ligands and a reduction of the valence state of the central Cu atoms.

**Keywords:** phthalocyanine, x-ray photoemission spectra, annealing, $Ar^+$ bombardment
**PACC:** 8120S, 3365F

## 1. Introduction

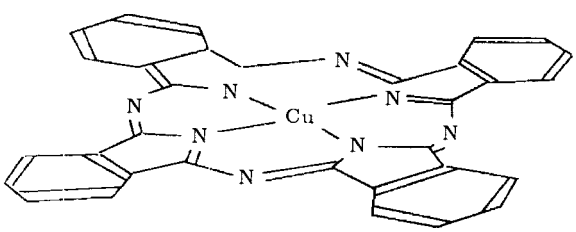
Phthalocyanine (Pc) compounds have attracted continued interest in recent years. They exhibit very interesting semiconducting,[1] catalytic[2] as well as nonlinear optical properties.[3] Moreover, for some metallophthalocyanine (MPc) compounds, the conductivity was found to be extremely sensitive to oxidizing gas contents. Therefore, they have a strong potential to be used as gas sensing detectors.[4] A review of the relevant research on MPc can be found, for instance, in the book by Simon and Andre.[5]

Pcs are a class of highly stable organic and/or organometallic compounds. Metal-free Pc ($H_2Pc$) is a planar aromatic system consisting of four isoindole units linked by aza nitrogen atoms. The two central hydrogen atoms can be replaced by a single divalent atom, such as Mg or Cu, Fe and other transition metal elements and their oxides. The molecular structures of the system are well known,[5] however the electronic structures have been the subject of numerous recent investigations, both theoretical and experimental. In particular, copper phthalocyanine (CuPc) is a p-type organic semiconductor, which has been applied as a gas sensor because its electrical conductivity is very sensitive to the adsorption of oxidizing gas. The sensitivity and selectivity can be modified by substituting the functional groups of CuPc either on its ring structure or on the sites of the central copper atom. It is also known that the structure and morphology of CuPc thin films strongly influence their gas-sensing characteristics.[6−10] Recently, Murakami and co-workers[11] have systematically studied the structural dependence of the gas-sensing property by investigating the films deposited at a variety of substrate temperatures. As a follow-up, in the present paper, we report on our work on CuPc grown on vanadyl phthalocyanine (VOPc) or titanyl phthalocyanine (TiOPc), in the form of a "twin-layer" structure. We present a detailed study of such twin-layer systems, such as their gas sensing behaviours and their stability in terms of thermal annealing as well as $Ar^+$ bombardment.

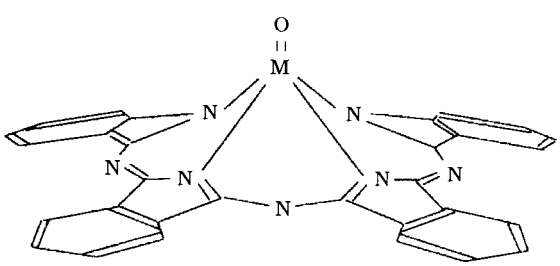
## 2. Experimental details

The $\alpha$-form CuPc films were prepared by the vacuum sublimation technique on glass substrates with

VOPc or TiOPc as the buffer layer. The substrates were kept at room temperature. The twin-layer structures were prepared by first depositing 200nm of VOPc or TiOPc, followed by the deposition of 200nm of CuPc films. The thickness of the films was measured using a quartz monitor. The details of the sample preparation can be found elsewhere.[12] The x-ray photoemission (XPS) spectra were taken using a Mark II VG ESCA lab, with a Mg $K_\alpha$ non-monochromatic source. The pass energy is typically 20eV, with an energy resolution of about 0.8eV. As-grown samples were studied first, followed by either in vacuo annealing for 30 min with a base pressure of $1\times10^{-7}$Pa or $Ar^+$ bombardment of different durations (Ar base pressure $1\times10^{-4}$Pa, kinetic energy 1keV). The MPc samples grown on glass substrates were not sufficiently conductive, thereby sometimes causing a charging effect during XPS measurements. As an organic semiconductor, the Fermi levels of the samples may also be variable depending on the active doping level of the samples under investigation. For comparison, in the present work, we have used the main peak of C 1s as the marker for aligning the XPS spectra. This will no doubt have its own inaccuracies but, for the present work, is sufficient to provide an overall picture. The crystalline structure was examined by an x-ray diffractometer, and the surface morphology by an atomic force microscope.




(a) CuPc




(b) MOPc($M$=$V$, Ti)

**Fig.1.** Schematic drawings of the molecular structures of (a) CuPc ($CuC_{32}H_{16}N_8$) and (b) MOPc ($MOC_{32}H_{16}N_8$, where $M = V$, Ti).

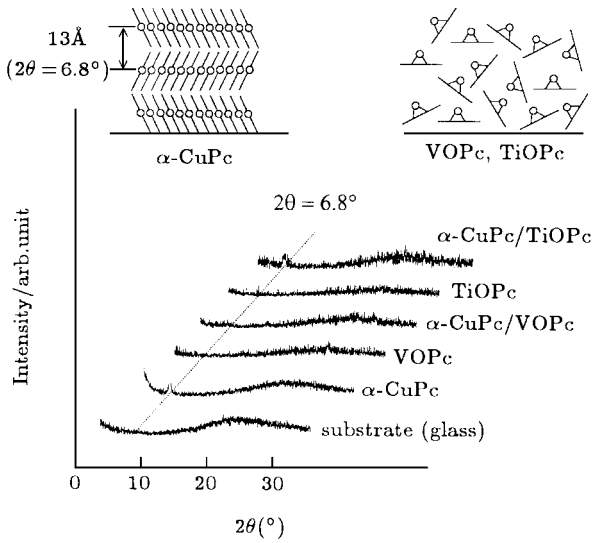



**Fig.2.** Low-angle XRD curves of MPc films. The inset shows schematically the structures of ordered $\alpha$-CuPc films and the amorphous-like VOPc and TiOPc films.

# 3. Results and discussion

## 3.1. Structure and morphology

As schematically shown in Fig.1, for CuPc the central Cu atom has an in-plane arrangement with the macrocyclic ring, whilst for both VOPc and TiOPc the central atoms have an out-of-plane arrangement. The x-ray diffraction (XRD) profiles are shown in Fig.2. As clearly seen from the diagram, the direct growth of CuPc onto glass substrates resulted in the formation of $\alpha$-CuPc in this case, which is characterized by the (200) diffraction peak at $2\theta$=6.8°, similar to those reported.[13] Both VOPc and TiOPc films showed amorphous-like structures. Subsequent growth of CuPc overlayers, however, indicated the formation of the $\alpha$ structure arrangement to a certain degree. The insets of Fig.2 illustrate schematically the structures of ordered $\alpha$-CuPc and the disordered VOPc and TiOPc films. Very interestingly, the specimens of twin-layer structures showed somewhat different characteristic responses to the oxidizing gas $NO_2$, as displayed in Fig.3, where the sensitivity was defined to be the change of conductance per unit increment of gas concentration. The twin-layer containing TiOPc showed a relatively lower sensitivity towards $NO_2$ exposure, whilst the twin-layer with VOPc showed a remarkable (approximately seven times greater) improvement of the performance. Atomic force mi-

croscopy (AFM) has been used to investigate the surface morphology of the films. All the films showed clustered surface morphology with a typical in-plane cluster dimension of 100nm and a typical height of less than 5nm.

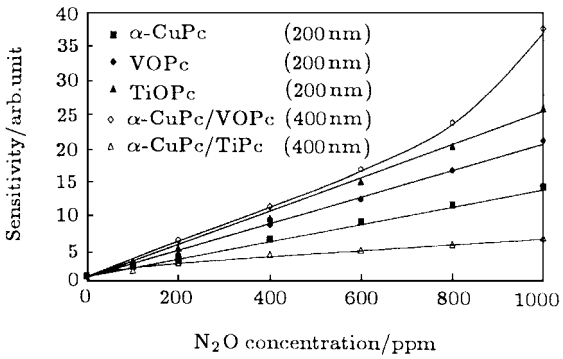



**Fig.3.** The sensitivity of the films towards $NO_2$ gas sensing.

### 3.2. X-ray photoemission spectra

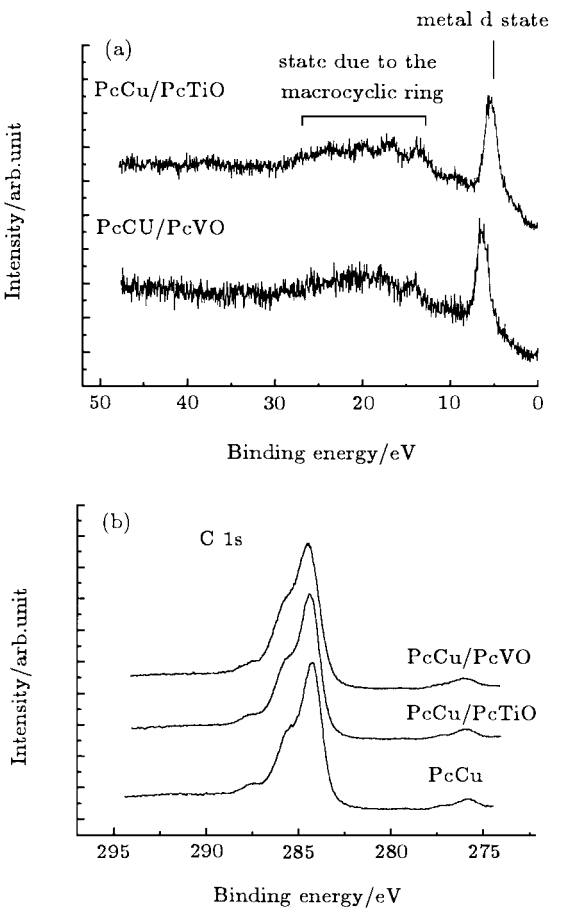



**Fig.4.** XPS spectra of the twin-layer structures of CuPc/TiOPc and CuPc/VOPc for (a) the valence band energy range and (b) the core level of C 1s. Both spectra show remarkable similarity to CuPc films.[14,15]

The XPS technique has been used to examine three aspects: the core and valence spectra of the as-grown samples, the thermal stability and the effects of $Ar^+$ bombardment on the twin-layer systems.

Figure 4(a) shows the valence band spectra of the CuPc/VOPc and CuPc/TiOPc twin-layer systems. It is well known, for phthalocyanine compounds, that the x-ray photoemission spectrum in the valence band region is characterized by a pronounced peak at lower binding energies due to the central metal d electron states, followed by additional features extended up to about 30eV. These additional features arise from the states in the macrocyclic ring and are similar to the superposition of XPS spectra of pyrrole and benzene.[14] The pronounced feature at lower energies, however, is dependent on the electronic states of the metal atoms. With a 200nm thick CuPc overlayer, and taking into consideration the sizes of clusters from AFM results, it is not surprising that both CuPc/VOPc and CuPc/TiOPc twin-layers showed essentially the characteristic spectra of CuPc valence band. As another example, in Fig.4(b), the C 1s core level spectra were shown for both CuPc grown on glass substrates as well as for the two twin-layer structures. There are two kinds of carbon atoms in metallophthalocyanines, namely 8 carbon atoms bonding to two nitrogen atoms and 24 carbon atoms of aromatic hydrocarbon character. The C 1s spectra were very much similar to those reported earlier.[15] The main peak has been attributed to the carbon of aromatic hydrocarbon character, the intermediate binding energy peak to the carbon bonding with two nitrogen atoms and possible contribution from the satellite of the main peak, and the higher binding energy peak to the satellite of the intermediate energy peak. The satellite peak is believed to be inherent of compounds such as phthalocyanines, a point we return to later in the paper. It is also known that the carbon spectra are insensitive to a type of central metallic atoms. Our XPS spectra of the twin-layer systems were found to be in general agreement with those of CuPc films previously reported.[14–15] While the overall spectra of the twin-layers, both core levels and valence band, illustrated CuPc characteristics, however we have been able to identify weak spectra due to Ti and V core electrons. In Fig.5(a), a weak Ti 2p core level spectrum of a CuPc/TiOPc twin-layer is displayed. Figure 5(b) shows the V 2p core spectra. The upper curve is taken from as-grown sample surfaces, where the V 2p features are just about visible. The lower

curve shows the spectrum obtained after 1 min $Ar^+$ cleaning, where the V 2p is more clearly observable. Of course, $Ar^+$ bombardment would cause damage to the sample structure as is fully discussed later. Nevertheless, this does not alter the fact that V-containing species were observed at and near the surfaces of the twin-layer structures. A thickness of 200nm of the CuPc overlayer is equivalent to well over a hundred monolayers of CuPc. Even taking into consideration the clustered surface morphology, it would be very unlikely that the XPS was probing the regions of TiOPc or VOPc not covered by CuPc overlayers. The presence of Ti or V at the surfaces of the twin-layer systems as detected by XPS is a clear indication that molecular migrations of Ti species or V species have occurred during or after the sample growth. The very existence of such migrated species may be one of the reasons for the different gas sensing responses of these twin-layer systems, mentioned earlier.

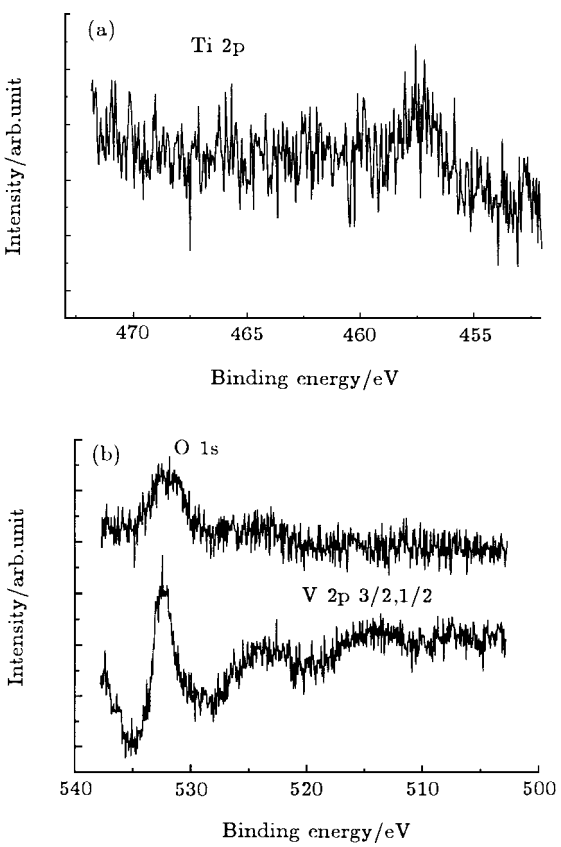



**Fig.5.** (a) Ti 2p core level spectrum of CuPc/TiOPc twin-layers and (b) V 2p core level spectra of CuPc/VOPc twin-layers. The upper curve was taken from as-grown CuPc/VOPc twin-layer surfaces, while the lower curve after 1 min of $Ar^+$ cleaning. The results indicate the existence of possible molecular migrations from the underlying layer to the surface.

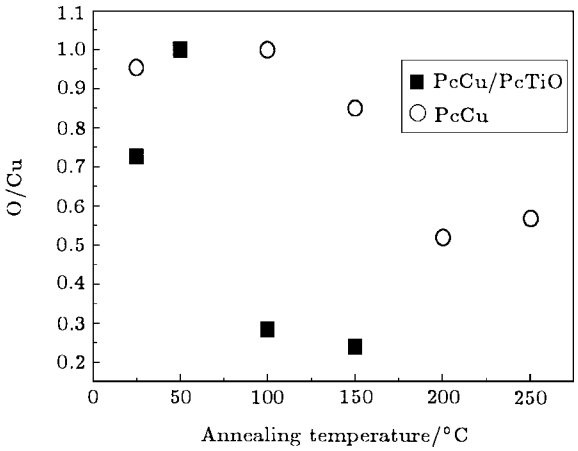



**Fig.6.** The loss of oxygen content as a function of annealing temperature for CuPc films directly grown on glass substrates and CuPc/TiOPc twin-layers. The oxygen 1s intensity is normalized against the corresponding Cu 2p intensity.

Now we examine the thermal stability of the twin-layer systems. It is well known that MPcs have high thermal stability. For instance, CuPc can be thermally sublimed at about 500°C without degrading the compounds. We have carried out preliminary thermal annealing studies of the twin-layer systems up to a maximum temperature of 250°C, under ultra-high vacuum (UHV) conditions. As indeed found in our XPS spectra, no measurable changes of the valence band N 1s, Cu 2p and C 1s core levels have been observed. We have also observed no measurable changes in the peak intensity of the Ti and V core levels, indicating that within the investigated temperature range, no further outwards migration of TiOPc or VOPc species occurred. One interesting aspect we have observed is the loss of adsorbed oxygen content during annealing. Figure 6 shows such data of oxygen loss. In order to avoid variations due to possible misalignment of the sample during measurements at different stages of annealing, the oxygen peak intensity is normalized against the Cu $2p_{1/2}$ core level intensity. As we can see from the diagram, during the annealing process, samples of CuPc directly grown on glass and CuPc/TiOPc twin-layers all showed the tendency of loss of adsorbed oxygen. For CuPc/TiOPc, the loss of the oxygen content occurred at lower temperatures and was more drastic. The oxidation and reduction of MPc can occur at the macrocyclic ring or the metal or both, depending on the particular type of central atoms. For CuPc it is known that the oxidation/reduction process takes place preferentially at the macrocyclic ring.[16] This may be the reason that,

despite the measurable loss of oxygen, no changes of the Cu 2p core levels have been observed. We have also found that during the annealing process the Ti binding energies decreased by an order of one electron volt, indicating that the Ti atoms in the migrated TiOPc species were being reduced. It is however not clear whether the existence of the migrated species acted as a catalysis to the enhancement of oxygen loss. A similar investigation of CuPc/VOPc twin-layers is currently being conducted. It would appear that the existence of either TiOPc or VOPc migrated species might play a role in the influence of the gas sensing characteristics of the twin-layer systems, and the oxygen desorption processes. Their correlation with the transport behaviour[4] certainly warrants a systematic investigation to provide a better understanding of the processes. Figure 7 shows the change of the Ti 2p core level binding energy as a function of annealing temperature for CuPc/TiOPc.

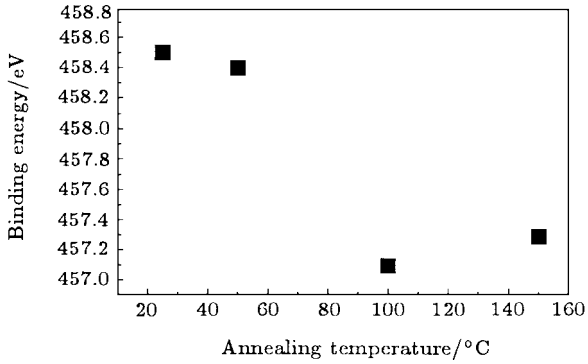



**Fig.7.** The shift of the Ti 2p binding energy as a function of annealing temperature.

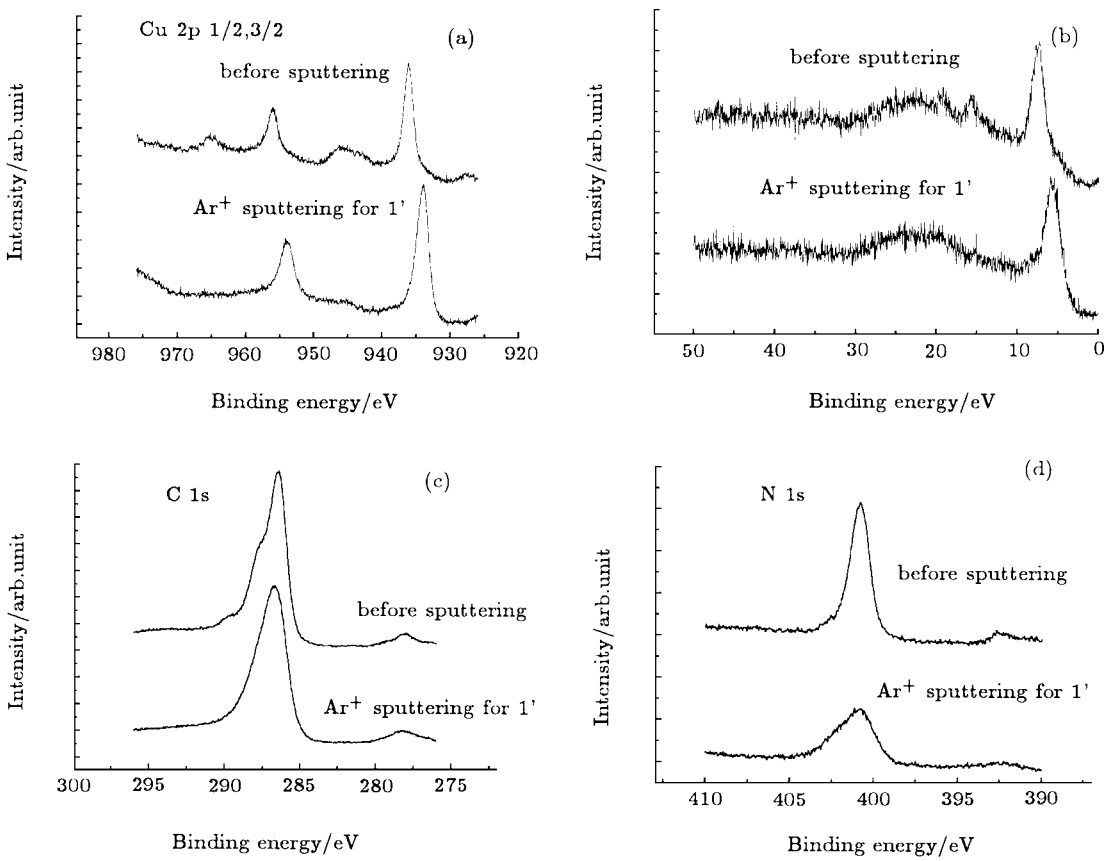



**Fig.8.** Comparison of XPS spectra of pristine CuPc/VOPc twin-layers and those at different stages of $Ar^+$ bombardment: (a) Cu 2p core level spectra; (b) valence band; (c) C 1s; and (d) N 1s core level spectra.

The CuPc films were found to be sensitive to $Ar^+$ bombardment. Argon ions caused considerable damage to the molecular structure of the metallophthalocyanines for all three structures we have studied. As an example, Fig.8 shows a comparison of typical XPS spectra before and after different stages of $Ar^+$ bombardment for the twin-layer structure of CuPc/VOPc. The changes induced by the bombardment can be

clearly identified. The damages by $Ar^+$ are twofold. From the Cu 2p spectra (Fig.8(a)), it can be seen that the bombardment caused a reduction of Cu II valence states to eventually Cu I or $Cu^0$ states. This was characterized by the suppression of the Cu 2p shake-up satellites and a shift of Cu 2p to lower binding energies.[17] Figure 8(b) shows the changes in the valence spectra. Whilst the main peak due to the Cu d states at lower binding energies remained, the additional features due to the macrocyclic ring at higher energies up to 30eV completely disappeared. This is a clear indication that the $Ar^+$ bombardment caused substantial damage to the macrocyclic ring structure. Evidence of the damage to the macrocyclic ring can also be found in the C 1s and N 1s spectra as both spectra have been altered considerably. For the C 1s spectra, in addition to the disappearance of the clear distinction of the three components, the high binding energy satellite peak was also suppressed. N 1s also showed a considerable broadening after $Ar^+$ bombardment.

## 4. Conclusion

To summarize, the twin-layer structures of CuPc/VOPc and CuPc/TiOPc showed remarkable differences in terms of gas sensing characteristics. XRD results showed that the buffer layers of VOPc and TiOPc were amorphous, whilst the subsequently grown CuPc overlayer was found, to a certain degree, to be in the $\alpha$-form crystalline structure. The XPS investigation of the as-grown samples revealed the molecular migration of the VOPc and TiOPc species into the surface regions of the thin films. The existence of such migrated species may be one of the causes for the different gas sensing behaviours. These two types of twin-layer structures have also been subjected to thermal annealing and $Ar^+$ bombardment. The structures were found to be fairly stable under thermal annealing.

However we have noticed that the oxygen desorption was somewhat different for the CuPc films grown directly on glass substrates and the twin-layer structures. It is not yet clear at the present stage as to whether or not the migrated species play any catalytic roles in the desorption process. We also found that the migrated TiOPc showed a decrease of Ti core level binding energies during the annealing process. Unlike CuPc where oxidation/reduction occurred preferentially to the macrocyclic ring, the reduction appeared to have happened to the central Ti atoms. Argon ion bombardment had induced considerable damage to both the twin-layer systems and the CuPc films grown directly on glass substrates. The damages were characterized by a reduction of the central Cu II atoms and the destruction of the macrocyclic rings. Further studies are underway to investigate systematically the effects of annealing and $Ar^+$ damage and the gas sensing behaviour of the twin-layer systems.

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## References

[1] Meier H 1974 *Organic Semiconductors* (Weinheim: Verlag Chemie)
[2] Fischer H, Schulz Ekloff G and Wohrle D 1997 *Chem. Eng. Technol.* **20** 624
[3] Yamashita A, Matsumoto S, Sakata S, Hayashi T and Kanbara H 1998 *J. Phys. Chem.* B **102** 5165
[4] Zhou Q and Gould R D 1998 *Thin Solid Films* **317** 432
[5] Simon J and Andre J-J 1985 *Molecular Semiconductors* eds Lehn J M and Rees Ch W (Berlin: Spinger-Verlag)
[6] Chadwick A V, Dunning P B M and Wright J D 1986 *Mol. Cryst. Liq. Cryst.* **134** 137
[7] Pizzini S, Timo G L, Beghi M, Butta N and Mari C M 1989 *Sensors Actuators* **17** 481
[8] Wright J D 1989 *Prog. Surf. Sci.* **31** 1
[9] Sadaoka Y, Matsugachi M, Sakai Y, Mori Y and Gopel W 1990 *J. Mater. Sci.* **25** 5257
[10] Dogo S, Germain J-P, Maleysson C and Pauly A 1992 *Thin Solid Films* **219** 251
[11] Nagasawa T, Takeuchi N, Murakami K and Watanabe K 1996 *Bull. Res. Inst. Electron. Shizuoka Univ.* **31** 99 (in Japanese)
[12] Nagasawa T, Murakami K and Watanabe K 1998 *Mater. Res. Soc. Symp. Proc.* **488** 329
[13] Debe M K and Kam K K 1990 *Thin Solid Films* **186** 289
[14] Hochst H, Goldmann A, Hufner S and Malter H 1976 *Phys. Status Solidi* b **75** 559
[15] Niwa Y, Kobayashi H and Tsuchiya T 1974 *J. Chem. Phys.* **60** 799
[16] Wolberg A and Manassen J 1970 *J. Amer. Chem. Soc.* **92** 2982
[17] Barr T L 1982 *Surf. Interface Anal.* **4** 185