Deposition of PbPc Thin Films Assisted by Argon Plasma of Electron Cyclotron Resonance Source

V.Sh. Aliev, I.A. Badmaeva*, L.D. Pokrovsky*, and A.S. Vasilyev*

Institute of Semiconductor Physics SB RAS, Novosibirsk, 630090, Russia
Phone: +8(383) 330-69-44, Fax: +8(383) 333-27-71, E-mail: aliev@thermo.isp.nsc.ru
**Institute of Semiconductor Physics SB RAS, Novosibirsk, 630090, Russia*

Abstract – Metal phthalocyanines are organic semiconductors, which find applications in the field of gas sensor, non-linear optics and molecular electronics. Lead phthalocyanine (PbPc) is of high interest owing to the quasi-one-dimensional conductivity and the electrical induced switching behavior for the monoclinic phase. It is well known that the monoclinic phase of PbPc is appeared only at low rate-growth and low not exceeded room substrate temperature. Increase in the rate-growth or substrate temperature results in the transition to the triclinic phase growth. For synthesis of the monoclinic phase films and improvement of the PbPc molecular deposition researchers are restricted within narrow limits of experimental parameters. In this paper an opportunity of the control of the crystal structure of PbPc films by means assisting of deposition process by argon plasma of electron cyclotron resonance (ECR) source has been investigated. The structure and surface morphology were controlled by AFM and RHEED. The triclinic and monoclinic phases were obtained at various ECR plasma assisting conditions.

1. Introduction

The phthalocyanines are a class of organic materials that have many unique properties [1] and that can be interesting for application in molecular electronics [2, 3], solar cells [4] and gas sensors [5]. Studies of the lead phthalocyanine (PbPc) take up special emphasis because of its structural and electrical properties [6–8]. Opposite to other metal phthalocyanine complexes, the PbPc molecules are non-planar and have shuttlecock shape. PbPc crystallize in two polymorphic phases: monoclinic and triclinic [6]. These two phases differ from each other in the stacking order of the molecules. The stacking order causes the high differences in electronic behavior of these phases. Only in monoclinic phase a crystal consists of columnar stacks of PbPc molecules with the interatomic distance between lead atoms 0.373 nm so that is slightly larger than the interdistance of ions in metallic lead (0.348 nm) [9]. Due to this particular way of stacking, PbPc in monoclinic phase is usually referred to as a typical one-dimensional conductor [10, 11], and a DC electrical conductivity along the stacking axis of the monoclinic phase is several orders of magnitude higher than that typical of the triclinic phase [12]. This feature of monoclinic phase makes it much more desirable for application. A phase composition and surface morphology of PbPc films vastly dependences on growth conditions [13–15]. The effect of deposition temperature and postdeposition annealing temperature on film structure has been studied in papers [15, 16]. The influence of deposition rate on the structure of grown films has been showed in paper [13]. On the other hand, it is common knowledge that the metal phthalocyanines are possessed superior chemical and thermal stability among organic substances. So, it is interesting to use a cold plasma treatment, which common and well-development applied in microelectronics, for the effect on the growth of PbPc films. Modification of surface properties of PbPc tetracarboxylic acid films by treated with ECR H_2/N_2 plasma and reactive ion etching of copper phthalocyanine films were early examined in papers [17, 18]. But these plasmas treatments were as postdeposition processes. In this paper, we investigated an opportunity of the control of the crystal structure of PbPc films by means assisting of deposition process with argon plasma of an electron cyclotron resonance (ECR) source.

2. Experiment

Commercial PbPc powder purified by repeated vacuum sublimation was loaded in effusion cell. The cell and 2.45 GHz microwave ECR plasma source were located in a vacuum chamber pumped with a turbomolecular pump to about 10^{-4} Pa. The evaporation rate and film thickness were controlled by a quartz crystal microbalance monitor from MAXTEC. Inc. However, this control was ability only at off-state of plasma source power. The terminal film thickness was measured by the ellipsometry. The molecular flow of PbPc was presetting by the sell temperature and maintain constant in all experiments. Plasma density was assign a value of *RF* power (P_{RF}) of the plasma source. Argon (Ar) 99.995% purity gas was use as generative gas of the plasma source. The vacuum pressure in the chamber at feeding Ar gas at deposition and plasma assisting processes was about $8.7 \cdot 10^{-3}$ Pa. The PbPc films were deposited on Si(100) substrates, which before loaded in the vacuum chamber passed through RCA cleaning procedure and after – *in-situ* ion beam cleaning in Ar ECR plasma. The films were deposited at room temperature; it was tested that substrate heating at deposition and plasma assisting process was

negligible. The ion energy distribution near the substrate was ranged from zero to 30 eV and for removed the distribution to higher energy range a negative electrical bias (U_b) was supplied on the Si substrate.

The surface morphology of PbPc films was characterized by using atomic force microscopy (AFM). AFM measurements were done with a SOLVER P-4 (NT-MDT) microscope operating in the trapping mode. An investigation of the crystalline structure of samples was carried out the reflection high-energy electron diffraction method (RHEED) using EF-Z4 installation with 50 kV accelerating voltage.

3. Results and discussion

The results of RHEED pattern identification were performed in Table 1. The strong intensity RHEED line for initial PbPc films is conformed to reflection from (800) plane with interplanar distance $d = 3.2$ A and that is pointed to monoclinic phase texture with the axis of molecular stacking directed toward perpendicular the plane of the Si surface. The reflection line with ($h\ k\ l$) = (300) and $d = 4.08$ A shown that portion of volume of films is occupied by the triclinic phase crystallite. The thickness of initial films was about 40 nm. After annealing in vacuum the films at temperature 125÷220 °C we observed diminution of film thickness and conservation triclinic phase share of films. It is known that evaporation temperature of monoclinic phase is about 340 °C, but it for triclinic phase is only 190 °C [15]. So, the identification of RHEED patterns confirms the results of paper [15]: the annealing leads to the monoclinic – triclinic transition and evaporating the triclinic phase from the film. It is interestingly note that the orientation of triclinic phase crystallites was varied at annealing. In initial films, the middle-strong intensity line was watched for the (300) plane and the (400) plane is not observed. At annealing the film the (300) plane line was slacken and the (400) plane line was became middle-strong intensity. Since monoclinic phase textures oriented by the Si surface plane so the triclinic phase crystallites formed at the monoclinic – triclinic transition grow in another orientation then at growth of the initial film.

The surface morphology of initial films is showed in Fig. 1.

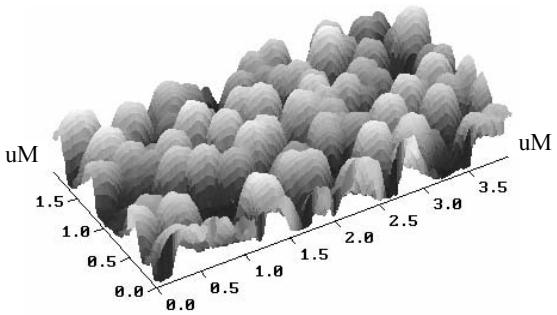

Fig. 1. The surface morphology of PbPc film on Si(100) grown at room temperature

We can observe cylindrical crystallites of about 500 nm in diameter, which oriented by its axis perpendicularly to the surface of the Si substrate. A dramatic change in surface morphology was watched after the annealing the film at 170 °C/2 h in vacuum (Fig. 2).

The cylindrical crystallites were destroyed and rugged relief was formed. Apparently, this morphology evolution was a consequence of conversion of the monoclinic phase to triclinic phase crystallites and evaporation of the last.

We used five modes of operation for ECR plasma assisting growth of PbPc films (Table 2).

A weak influence upon the growth in L operation mode of assisting decreases a monoclinic phase growth and increases a triclinic phase share, probably, because of ion-induced monoclinic – triclinic phase transition, likely thermal induced transition as described above.

Table 1. RHEED pattern identification

Monoclinic phase [15, 19]		Triclinic phase [15, 19]		Initial film (unannealed)		Annealed temperature, °C					
						125		170		220	
h k l	*d*, A	*h k l*	*d*, A	*d*, A	*I*	*d*, A	*I*	*d*, A	*I*	*d*, A	*I*
200	12.78	100	11.87								
320	6.98	020	7.27	7.9	*BB*, vw	7.5–7.9	*BB*, vw	7.5–7.9	*BB*, vw	7.5–7.9	*BB*, vw
420	5.34					5.25	w	5.25	w	5.5	w
		200	5.92								
		300	3.95	4.08	*T*, m-s	4.02	*T*, m-s	4.02	*T*, w	4.08	*T*, w
111	3.68			3.67	m-s	3.76	m-s	3.76	m-s	3.70	str
800	3.2*			3.25	*T*, str	3.25	*T*, str	3.20	*T*, str	3.29	*T*, str
		400	2.95			2.86	vw	3.04	vw	2.98	*T*, m-s
840	2.67*									2.70–2.78	*T*, str

N o t e . Shorthand notation: *BB* – broad band line; *T* – textured film; vw – very weak; w – weak; m – middle; m-s – middle-strong; str – strong intensity RHEED line; * – this reflections are not in data of papers [15, 19]; *d* – the interplanar distance in angstrom unit, A; *I* – shape and intensity of the reflection line.

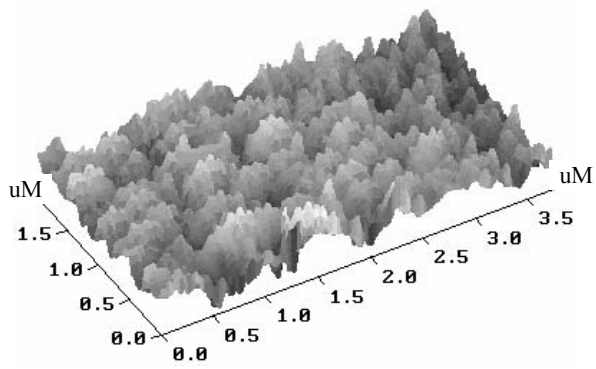

Fig. 2. The surface morphology of PbPc film, showed on Fig. 1, annealed at 170 °C temperature in vacuum condition during 2 h

Table 2. Dynamics of changes of the phase composition of PbPc films grown at variety operation modes of Ar ECR plasma assisting

Label of operation mode	Parameters of ECR plasma assisting		Phase mixture
	P_{RF}, W	U_b, V	
Without assisting	0 W	0 V	monoclinic + triclinic + amorphous
L	30 W	0 V	monoclinic ↓ + triclinic ↑ + amorphous ↑
M	50 W	0 V	amorphous
MS	50 W	–30 V	unknown phase + amorphous ↓
ST	50 W	–50 V	monoclinic ↑ + triclinic ↑ + amorphous ↓
P	100 W	–100 V	amorphous

Note. P_{RF} – a *RF* power of plasma source; U_b – a negative electrical bias supplied on the Si substrate; ↑ and ↓ – increasing and decreasing phase share, respectively.

In contrast to thermal induced transition, the operation temperature was low, and the evaporation did not take place so that is the result of an accumulation of triclinic phase share. Concurrently the growth of amorphous phase was watched. An augmentation of assisting effort up to M-mode resulted in the growth of amorphous film. The increase of ion energy nearby a growing layer by means supplied U_b (MS- and ST-modes) dramatically modified the growth mechanism. At the beginning, an unknown phase is appeared and then monoclinic and triclinic phases once again are grown. The RHEED pattern for ST mode showed more clear reflection lines than without assisting mode. Further more augmentation of values of P_{RF} and U_b (P-mode) resulted in formation of an amorphous film. It is significant that the films synthesized at P-mode were kept the amorphous state and thickness after vacuum annealing at 190 °C temperature. It can really be so if films were polymerized at the growth.

In conclusion at low intensity assisting operation modes (L, M) the Ar ECR plasma effects likely vacuum annealing. The increase of plasma assisting intensity destroys the molecular structure of organic crystallites without bond breaking into phthalocyanine molecules. The bond breaking processes occurs at the increase of ion energy (MS- and ST-modes). In this case, probably, new chemical components are appeared into plasma medium and a growth of molecular crystalline structures are possible again. However further the increase of the bond breaking processes (P-mode) stimulates polymerization of film.

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References

[1] R.D. Gould, Coordination Chem. Rev. **156**, 237 (1996).
[2] D. Campbell and R.A. Collins, Phys. Status Solidi A **152**, 431 (1995).
[3] J. Kaspar, I. Emmer, and R.A. Collins, Int. J. Electron. **76**, 793 (1994).
[4] E. Orti, J. Chem. Phys. **92**, 1228 (1990).
[5] Q. Zhou and R.D. Gould, Thin Solid Films **317**, 436 (1998).
[6] K. Ukei, K. Takamoto, and E. Kanda, Phys. Letters A **45**, 345 (1973).
[7] R.D. Gould and T.S. Shafai, Thin Solid Films **373**, 89–93 (2000).
[8] S. Ambily, F.P. Xavier, and C.S. Menon, Materials Lett. **41**, 5–8 (1999).
[9] K. Ukei, Acta Crystallogr. B **29**, 154 (1973).
[10] M. V. Symonyan, E.A. Kafadaryan, M.Ch. Nurijanyan, A.K. Petrosyan, and E.G. Sharoyan, Phys. Status Solidi A **101**, 143 (1987).
[11] Th. Frauenheim, C. Hamann, and M. Muller, Phys. Status Solidi A **86**, 735 (1984).
[12] Y. Iyechika, K. Yakushi, I. Ikemoto, and H. Kuroda, Acta Cryst. B **38**, 766 (1982).
[13] Y. Machida, Y. Saito, A. Taomoto, K. Nichogi, K. Waragai, and Sh. Asakawa, J. Appl. Phys. **28**(2), 297 (1989).
[14] L. Ottaviano, L. Lozzi, S. Santucci, S. Di Nardo, and M. Passacantando, Surface Sci. **392**, 52 (1997).
[15] L. Ottaviano, L. Lozzi, A.R. Phani, A. Ciattoni, S. Santucci, and S. Di Nardo, Appl. Surface Sci. **136**, 81 (1998).
[16] R.A. Collins and A. Belghachi, Mater. Lett. **8**, 349 (1989).
[17] M. Naddaf, S. Chakane, S. Jain, S.V. Bhoraskar, and A.B. Mandale, Nucl. Instr. & Meth. Phys. Res. B **194**, 54 (2002).
[18] G.L. Pakhomov, M.N. Drozdov, and N.V. Vostokov, Applied Surface Sci. **230**, 241 (2004).
[19] A. Miyamoto and K. Nichogi, Thin Solid Films **256**, 64 (1995).