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**THE EFFECT OF GRAVITY AXIS ORIENTATION ON THE GROWTH OF
PHTHALOCYANINE THIN FILMS**

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INTRODUCTION

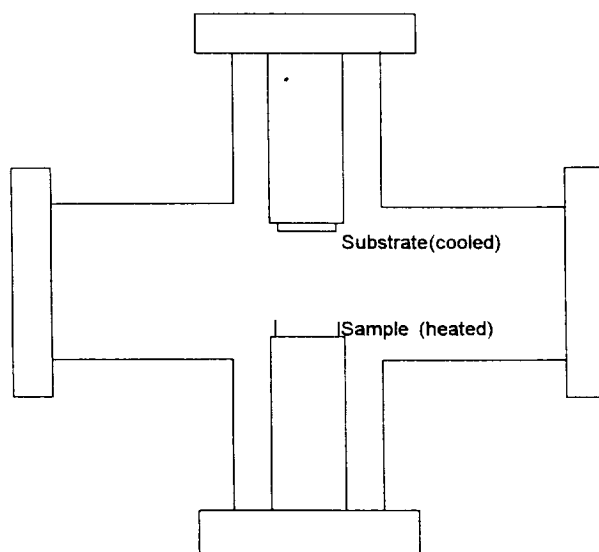
Experimentally, many of the functions of electrical circuits have been demonstrated using optical circuits and, in theory, all of these functions may be accomplished using optical devices made of nonlinear optical materials(1-5). Actual construction of nonlinear optical devices is one of the most active areas in all optical research being done at this instant(6-11).

Physical vapor transport (PVT) is a promising technique for production of thin films of a variety of organic and inorganic materials. Film optical quality, orientation of microcrystals, and thickness depends critically on type of material, pressure of buffer gas and temperature of deposition. An important but understudied influence on film characteristics is the effect of gravity-driven bouancy. Frazier, Hung, Paley, Penn and Long (12) have recently reported a mathematical modelling of the vapor deposition process and tested the predictions of the model on the thickness of films grown by PVT of 6-(2-methyl-4-nitroanilino)-2,4-hexadiyn-1-ol (DAMNA.)

In an historic experiment, Debe, et. al. (13,14) offered definitive proof that copper phthalocyanine films grown in a low gravity environment are denser and more ordered than those grown at 1 g. This work seeks to determine the influence on film quality of gravity driven bouancy in the low pressure PVT film growth of metal-free phthalocyanine.

EXPERIMENTAL

The vapor deposition cell used in this work is illustrated in Figure 1 below.



VAPOR DEPOSITION APPARATUS

FIGURE 1

The "top" segment of the cell contains the cold finger on which the quartz substrate is mounted. The phthalocyanine is contained in a heated graphite crucible located in the "bottom" segment. The cell is mounted inside the vacuum chamber by attachment through a rotatable flange on one of the "horizontal" segments which allowed the cell to be rotated 45° with respect to the vertical (gravity) axis. The inside of the of the apparatus is evacuated through an open observation port in one of the horizontal segments. The temperature of the cold finger is maintained at 5°C, a temperature found to yield highly ordered films of good optical quality. The temperature of the heater was set at 330°C which maintained the partial pressure of phthalocyanine at approximately 1×10^{-6} torr. The total pressure inside the cell was maintained at 1×10^{-2} torr using argon as a buffer gas. The deposition time was 2 hours.

RESULTS AND DISCUSSION

All the films appeared to be of good optical quality both visually and microscopically. The thickest film, judged by the intensity of the blue color, did appear to have scattering regions. Microscopically, these regions had the appearance of tiny "needles" composed of much smaller microcrystals covering the surface. All the films showed some imperfections consisting of crystalline "clusters", and some larger crystal segments. These imperfections will act as scattering centers and may limit the performance of such films in optical devices.

Electron microscopy was able to resolve the fine details of the film. The film grown vertically showed a more uniform appearance but appeared to be less dense. The needles on the surface were smaller and less numerous than those grown at 45°. The effect is probably due to the thinner vertically grown films.

The thickness of the films was measured by both ellipsometry and profilometry. The ellipsometer used a helium-neon laser source, wavelength 632.8 nm at 70° to the surface. The spot size was 0.025 x 0.086 mm and nine readings were taken on each film. The data is summarized in Table 1. All measurements are given in Angstrom units.

film number	orientation	maximum thickness	average thickness	minimum thickness	3 standard deviations
2	vertical	802	702	657	135
5	vertical	876	872	869	7
6	vertical	868	863	856	13
7	vertical	910	904	899	11
1	45°	915	890	875	36
3	45°	853	837	821	33
Average (vertical)		864	838	820	42
Average (45°)		884	864	848	34

TABLE 1

While there is considerable spread in the numbers, it is significant that all three values; the maximum thickness, the average thickness and the minimum thickness are thicker for the films grown at 45° relative to the gravity axis. The most troubling feature of the ellipsometer readings is that films #6 and #7 show thicknesses larger than or comparable to films #1, #2, and #3. The latter three films appear to be the thickest judged by the intensity of the color of the films whereas, the former two films are so faintly coated that almost no blue color is observable.

In view of the questionable readings obtained from ellipsometry, the film thickness was also measured by profilometry. The profilometer results are shown in Table 2. The thickness is measured in Angstrom units.

film #	orientation	thickness
2	vertical	350
5	vertical	185
6	vertical	70
7	vertical	75
1	45°	280
2	45°	410
	Average (vertical)	170
	Average (45°)	345

TABLE 2

The thickness found from profilometry are in the order expected judging from a visual observation of the colored films. These readings are inconsistent with the film thickness measured by ellipsometry. At present, there appears to be no obvious reason for the discrepancy. However, the profilometer readings also show that the films grown at 45° relative to the gravity axis are considerably thicker than those grown with the cell axis parallel to the gravity axis.

Since there is a discrepancy between the thickness measured by ellipsometry and that measured by profilometry that is greater than the uncertainty in either of the measurements, both these readings should be repeated using different instruments. Part of the problem may result from the fact that the films are too thin. The experiment should be repeated with experimental parameters which increases the film thickness.

There are three possible ways to increase the thickness of the films: the deposition time could be increased, the evaporation temperature could be increased, or the buffer gas pressure could be lowered. A more thorough study investigating the effect of pressure should be attempted. It is surprising that a pressure as low as 10^{-2} torr has such an effect on bouancy since the mean free path is long and gas density is low. An investigation to determine the minimum pressure at which gravity driven bouancy effects are measurable should be initiated.

Pressures above 10^{-2} torr will be difficult because the films will be even thinner than those of this study unless other parameters are adjusted.

It will be difficult to increase the evaporation temperature. The current heater was drawing more than 7.0 amps of current at 330°C . As viewed through the observation port, the leads connected to the heater were glowing at this current. Increasing the current may result in damage to the heater or nonuniform heating of the sample. The simplest way to increase the film thickness is to increase the deposition time. This will have the added benefit of producing a better quality thick film due to the slower deposition rate. The films will need to be about twice as thick in order to make meaningful comparisons between the thickest and the thinnest films. This will require about 4 hours of deposition time. It may be somewhat advantageous to increase the deposition time to 5 to 6 hours with a corresponding decrease in the evaporation temperature in order to protect the heater.

The films should be studied by x-ray diffraction in order to determine if gravity axis orientation has an influence on the degree of ordering of the microcrystalline film on the substrate surface. At 5°C condensation temperature, the most prominent reflection is 100 indicating significant ordering of crystal planes on the substrate surface. Nonlinear optical properties depend significantly on the extent of ordering in the films.

This study has shown that good quality films can be produced from metal-free phthalocyanine and that the film quality and thickness is affected by the orientation of the vapor deposition axis relative to the gravity axis. A rotation of 45° is observed to produce thicker films of lower quality than those grown vertically. Experimental difficulties related to the thin films obtained made it impossible to quantitate the effects. The results do indicate that a more detailed experiment is in order including comparison of films of the same thickness but grown at different orientations relative to the gravity axis. It is probable that the 45° orientation may produce better quality films of the same thickness than those grown parallel to the gravity axis.

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