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A REVIEW OF MELT AND VAPOR GROWTH TECHNIQUES FOR POLYDIACETYLENE THIN FILMS FOR NONLINEAR OPTICAL APPLICATIONS

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16. ABSTRACT

Methods for the growth of polydiacetylene thin films by melt and vapor growth and their subsequent polymerization are summarized. Films with random orientations were obtained when glass or quartz were used as substrates in the vapor growth process. Oriented polydiacetylene films were fabricated by the vapor deposition of diacetylene monomer onto oriented polydiacetylene on a glass substrate and its subsequent polymerization by UV light. A method for the growth of oriented thin films by a melt-shear growth process as well as a method of film growth by seeded recrystallization from the melt between glass plates, that may be applied to the growth of polydiacetylene films, are described. Moreover, a method is presented for the fabrication of single crystal thin films of polydiacetylenes by irradiation of the surface of diacetylene single crystals to a depth between 100 and 2000 Å.

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A REVIEW OF MELT AND VAPOR GROWTH TECHNIQUES FOR POLYDIACETYLENE THIN FILMS FOR NONLINEAR OPTICAL APPLICATIONS

I. INTRODUCTION

The polydiacetylenes, a class of fully-ordered polymeric single crystals, are very attractive materials for use in nonlinear applications and devices. Sauteret et al. [1] measured the cubic nonlinear effects in poly-toluene sulfonate and bis-phenyl urethane of 5,7 dodecadiyne-1,12-diol (TCDU) diacetylene single crystals at 1.89 μm fundamental wavelength and found values of $\chi^{(3)} = 7.0 \times 10^{-9}$ esu and $\chi^{(3)} = 8 \times 10^{-10}$ esu, respectively. These values of $\chi^{(3)}$ are of the same order of magnitude as those of Ge and GaAs which are 10^{-10} and 10^{-11} esu along the (111) direction [2].

To fully exploit their use in nonlinear optical devices, polydiacetylenes should be used as thin film waveguides. A desirable feature of thin film waveguides in comparison to bulk crystals is that they can maintain larger power densities over much longer propagation paths.

If we compare second harmonic conversion rates, η, by a bulk crystal (η_b), and a planar waveguide (η_{wg}), we may condense the resulting expression to [2]:

$$\eta_b \sim \lambda^{-1} L P^{(\omega)}$$

and

$$\eta_{wg} \sim a^{-2} L^2 P^{(\omega)}$$

where

λ = wavelength

L = crystalline length

$P^{(\omega)}$ = power to pump beam

a = waveguide thickness .

We see that η_b depends on total power whereas, η_{wg} depends on power density, P/a^2, and is quadratic with respect to the length of the crystal. If we assume that waveguide thickness is of the order of wavelength, i.e., $a \sim \lambda$, then

$$\frac{\eta_{wg}}{\eta_b} \sim \frac{L}{\lambda}$$

and for L = 1 cm and λ = 1 μm

$$\frac{\eta_{wg}}{\eta_b} \sim 10^4 \quad .$$

Hence, conversion rates theoretically favor the planar waveguide configuration by an order of 10^4. Although conversion efficiencies to quadratic effects are theoretically much better in waveguide than bulk crystal, to achieve the advantage film thickness must be very carefully controlled throughout the crystal length [3]. For this reason, the Langmuir-Blodgett (LB) process has been used to prepare polydiacetylene thin films [4]; however, this process is time-consuming and complicated and is limited to growth of surface active diacetylene monomers. Because of these deficiencies in the LB process, a research program has been established in this laboratory to fabricate polydiacetylene thin films by melt and vapor growth processes. There may be significant advantage to growing thin films by vapor growth in microgravity by avoiding unwanted fluctuations in temperature and flow at the growing crystal. Such avoidance could enhance constancy of film thickness, a critical parameter to help maximize conversion efficiency. This paper is a review of the scientific literature to establish a basis for the preparation of polydiacetylene thin films by melt and vapor growth.

II. THIN FILM GROWTH BY MELT PROCESSES

Thakur et al. [5-6] and Seymour [7] developed a method for the fabrication of thin film polydiacetylene single crystals that were approximately 1 cm^2 in area and 1 μ in thickness. The diacetylene monomers used in this study were 5,7-dodecadiyne-1, 12-diol-bisphenylurethane (TCDU), and 5,7-dodecadiyne-1,12-diol-bisethylurethane (ETCD) (Table 1). The principal steps of the method are as follows: (1) the diacetylene monomer was placed between two optically flat opposing surfaces and melted, (2) a suitable amount of pressure was applied to the substrate/monomer/substrate assembly, (3) the monomer melt under a constant pressure was subsequently subjected to shear by a linear slow translation of one of the substrates with respect to the other, and (4) the final step was to gradually reduce the temperature. The diacetylene thin film single crystals were polymerized by using established methods such as UV-irradiation or heat.

TABLE 1. DIACETYLENE MONOMERS USED TO PREPARE THIN FILM POLYDIACETYLENE SINGLE CRYSTALS BY A MELT SHEAR TECHNIQUE

Monomer	Side Group (R) of Diacetylene Monomer (R-C≡C-C-C≡C-R)
TCDU	$-(CH_2)_4-O-CO-NH-C_6H_5$
ETCD	$-(CH_2)_4-O-CO-NH-C_2H_5$

Berrehar et al. [8] described a method by which thin film polydiacetylene single crystals can be fabricated from bulk single crystals prepared by melt, vapor or solution growth processes. In this method, a diacetylene single crystal was cleaved along the desired plane and the surface was polymerized using electron irradiation. The film thickness which ranged between 100 and 2000 Å for a sample surface of a few tenths of cm^2 was controlled by adjusting the incident electron energy. In this study, the polymer film remained on the monomer substrate. It can be separated from it by selective dissolving of the monomer and transfer of the polymer film to an appropriate substrate [8]. The chemical formulae for diacetylene monomers used in this study are listed in Table 2.

TABLE 2. DIACETYLENE MONOMERS USED TO PREPARE THIN FILM POLYDIACETYLENE SINGLE CRYSTALS BY ELECTRON IRRADIATION OF THE SURFACE OF DIACETYLENE BULK SINGLE CRYSTALS

Monomer	Side Group (R) of Diacetylenes (R-C≡C-C≡C-R)
pTS	CH_3-C_6H_4-SO_4-CH_2-
pTS-12	CH_3-C_6H_4-SO_2-O-$(CH_2)_4$-
pFBS	F-C_6H_4-SO_2-O-CH_2-
TCDU	H-C_6H_4NHCOO-$(CH_2)_4$-

Ledoux et al. [9] used a melt growth process to prepare single-crystalline thin films of N-(4-nitrophenyl)-L-prolinol (NPP). The same process may be useful in preparing single-crystalline polydiacetylene thin films. The NPP films were prepared by placing a small amount of powder (2 mg) between a glass or silica microscope slide and cover slip that are separated by a Mylar or poly(vinylidene fluoride) ringlike spacer. The powder was carefully melted until only a small seed remained and then quickly cooled to about 1.5°C below the melting point where a small initiating crystal started to grow. The sample was maintained at this temperature for 10 hr and then cooled slowly until complete recrystallization was achieved. Thin film polydiacetylene single crystals could be grown using this method by first preparing diacetylene single crystals by the method summarized above followed by polymerization under UV, X-ray, γ-ray, or electron irradiation. 5,7-Dodecadiyne-1,12-diol-bisphenylurethane (TCDU) and 5,7-dodecadiyne-1,12-diol-bisethylurethane (ETCD) are examples of thermally stable diacetylene monomers that could be used to fabricate polydiacetylene thin films.

III. THIN FILMS BY VACUUM DEPOSITION

Tomaru et al. [10,11] prepared thin films of polydiacetylenes by vacuum deposition of a 1,6-di(alkylurethane)-2,4-hexadiyne monomer (see Table 3 for chemical structure) and 4,6-decadiyne-1,10-diol monomer onto glass followed by polymerization with UV irradiation. The growth conditions and $\chi^{(3)}$ values are summarized in Tables 3 and 4. The most important factor in fabricating polydiacetylene thin films by vacuum deposition was control of the evaporation temperature because the monomers

TABLE 3. VAPOR GROWTH CONDITIONS FOR POLYDIACETYLENE THIN FILMS PREPARED BY TOMARU ET AL. [10,11]

	Diacetylene Monomer	Substrate	Pressure (torr)	Evaporation Temperature (°C)	Substrate Temperature (°C)	Reference
(1)	1,6-di(alkylurethane)-2,4-hexadiyne $(-C\equiv C-CH_2-O-CO-NH-C_4H_9)_2$	Glass	10^{-5}	140	–	10
(2)	4,6-decadiyne 1,10 diol $HO-(CH_2)_3-C\equiv C-C\equiv C-(CH_2)_3-OH$	Glass	–	90-140	Room Temperature	11

TABLE 4. $\chi^{(3)}$ VALUES FOR POLYDIACETYLENE THIN FILMS PREPARED BY TOMARU ET AL. [10,11] BY VAPOR GROWTH PROCESSES

Diacetylene Monomer	χ^3 Value at 1.9 μm Wavelength	Reference
(1) 1,6-di(alkylurethane)-2,4-hexadiyne $(-C\equiv C-(CH_2)-O-CO-NH-C_4H_9)_2$	1.4×10^{-11} esu	10
(2) 4,6-decadiyne 1,10 diol $HO-(CH_2)_3-C\equiv C-C\equiv C-(CH_2)_3-OH$	1.1×10^{-11} esu (along polymer chain) $< 10^{-12}$ esu (across polymer chain)	11

may decompose or polymerize with excessive heat treatment. The evaporation temperatures for 4,6-dodecadiyne 1,10-diol and the 1,6-di(alkylurethane)-2,4-hexadiyne monomer were 90°to 140°C and 140°C, respectively.

Kanetake et al. [12,13] prepared films of poly[dodecadiyne-1,12-diol-bis(n-butoxycarbonyl-methyl-urethane)] [PDA-4BCMU] and 12-8 PDA (with side-group R = C_{12} H_{25}). To prepare films of 12-8 PDA, diacetylene monomer was deposited on glass or quartz plates then the monomer film was polymerized by UV light. Highly oriented films of PDA-4BCMU as large as several cm^2 were prepared using a new alignment technique. Purified monomer was loaded into a quartz pot and was heated in a vacuum of 6 x 10^{-6} Torr at about 125°C. The glass substrate was held at 10°C during the vacuum deposition process. The monomer film which had a thickness of a few hundred angstroms was then polymerized with UV light. The polymer film was stroked softly with silicon cloth along a fixed direction ot induce alignment of the polymer chains by shear stress. At this stage only a few molecular layers are supposed to remain on the substrate. The final step was vacuum deposition of a secondary monomer film upon the pretreated substrate and subsequent polymerization using UV light.

IV. CONCLUSION

Much work remains to be done in developing technology for the fabrication of polydiacetylene thin films by melt and vapor growth processes for use in nonlinear optical devices; however, the information presented in this paper provides a good basis for further work. Although glass and quartz were used as substrates for the growth of random oriented film, growth of highly oriented films might be achieved by using single crystalline substrates such as silicon. In addition, a detailed analysis of the effect of processing parameters on material properties would be useful in the development of optimum nonlinear optical devices. These areas of concern will be included in the research program that has been established in this laboratory.

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APPROVAL

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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

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