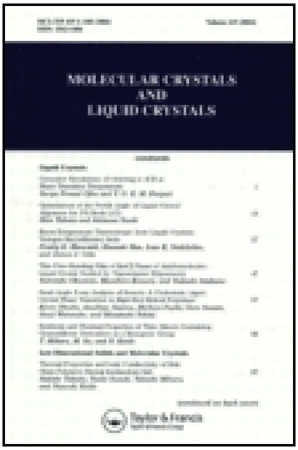

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Real-Time Spectroscopic Ellipsometric Studies of Photo-Assisted Chemical Processes

Ilsin An [a] , Hye-Keun Oh [a] & M. S. Paley [b]

[a] Department of Physics, Hanyang University, Ansan, 425-791, Korea

[b] The Space Science Laboratory, NASA Marshall Flight Center, Huntsville, Alabama, 35812, USA

Version of record first published: 24 Sep 2006

To cite this article: Ilsin An, Hye-Keun Oh & M. S. Paley (2001): Real-Time Spectroscopic Ellipsometric Studies of Photo-Assisted Chemical Processes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 371:1, 313-316

To link to this article: http://dx.doi.org/10.1080/10587250108024749

Mol. Cryst. and Liq. Cryst., 2001, Vol. 371, pp. 313-316

Real-Time Spectroscopic Ellipsometric Studies of Photo-Assisted Chemical Processes

ILSIN AN[a], HYE-KEUN OH[a] and M.S. PALEY[b]

[a] *Department of Physics, Hanyang University, Ansan, 425-791, Korea and* [b] *The Space Science Laboratory, NASA Marshall Flight Center, Huntsville, Alabama 35812, USA*

Real-time spectroscopic ellipsometry was employed to characterize the photo-assisted growth of polydiacetylene films in solution. From regression analysis, the low growth rate of ~3 Å/min was obtained and the reduction of growth rate due to absorbing film was observed. The growth was strongly affected by the movement of solution indicating a reaction-limited process at film and solution boundary.

Keywords ellipsometry, polydiacetylene, photo-assisted

INTRODUCTION

Ellipsometry has been successfully used in many thin film processes. Due to the limited data acquisition speed, spectroscopic ellipsometry has been applied to the characterization of the optical properties or microstructural properties of static surfaces [1, 2]. Meanwhile, single wavelength ellipsometry has been applied to the growth or modification processes of thin films [3, 4]. Recently, however, real-time spectroscopic ellipsometry (RTSE) has been realized thanks to the multichannel detection system such as photodiode array and charged coupled device. The major successful application of RTSE was in the field of vacuum growth of thin films [5-7]. Only few works were performed on electrochemical processes [8]. Compared to the vacuum

processes where the optical properties of most materials are well known and the optical structures of materials are not so complex, the chemical processes are too complex to perform and to analyze.
Recently, a novel photo-assisted process was developed to deposit thin amorphous polydiacetylene films from monomer solution onto transparent substrates [9]. Polydiacetylene is highly conjugated organic polymers, which have potential applications in organic conductors, semiconductors and nonlinear optical material. Although relatively high quality thin films were acquired with this process compared to spin coating or Langmuir-Blogett technique, more efforts are needed to understand the growth mechanism. For device applications, the growth rate needs to be increased and the use of other substrate rather than UV transparent glass should be considered. We applied RTSE to the deposition of polydiacetylene thin film in order to understand the photo-assisted growth process.

EXPERIMENTAL

The photochemical cell was designed in such a way that UV light reaches the substrate from the backside and probing ellipsometry beam travels the substrate from the front surface at an angle of incidence 60 degree through fused silica windows as shown in FIG. 1.

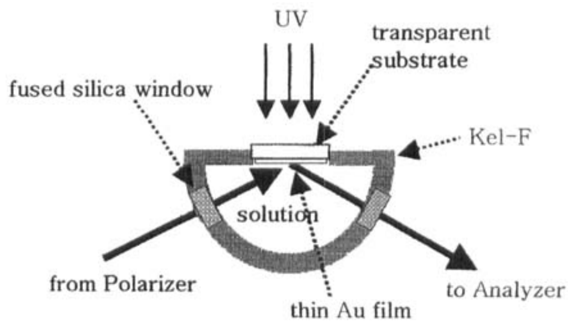

FIGURE 1. Schematic of photochemical cell used in the study.

For ellipsometric measurements very thin (~80 Å) gold film was thermally evaporated onto the fused silica substrate to enhance the sensitivity at the expense of UV transmission. As the reflection from the backside of substrate is non-coherent, thick substrate and pinhole were used to separate the reflections from both sides of substrate.

DATA ANALYSIS AND DISCUSSION

For solution, monomer of 2-methyl-4-nitroaniline diacetylene was dissolved in 1, 2-dichloroethane using sonification method [10]. This solution filled the photochemical cell shown in Fig. 1 and ellipsometry spectrum was taken every 30 sec during UV exposure for several hours. UV exposure was provided by 15 W Hg lamp without wavelength selection. We stirred the solution in the middle of the growth of polydiacetylene film to see the effect of disturbance. The typical data obtained in this work is shown in Fig. 2 (a). The $\Delta_{exp}(h\nu)$, $\Psi_{exp}(h\nu)$ spectra at time t=0 shows the substrate, 80 Å Au on fused silica. The plateau between t=110 and 180 min is visible, which is caused by stirring of solution.

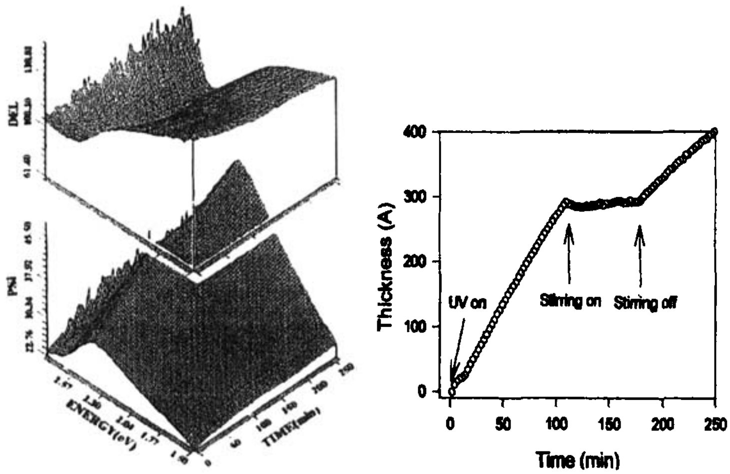

FIGURE 2. (a) Three dimensional RTSE data consisting of 500 $\Delta_{exp}(h\nu)$, $\Psi_{exp}(h\nu)$ spectra. (b) Evolution of thickness, d(t), obtained from regression analysis using a single layer model.

Time evolutions of data become more vivid if we select one pair of Δ_{exp}, Ψ_{exp} corresponding to a specific photon energy from each spectrum in Fig. 2 (a). From RTSE data, thickness, d is obtained as a function of time as shown in Fig. 2 (b) using regression analysis with a single layer optical model. The analyzed results in Fig. 2 (b) show growth rate and the change of growth rate quantitatively. From the slope of first 110 mins, we can estimate the growth rate of 3 Å/min. The stopped growth during the stirring of solution between 110 min and 180 min indicates that there is a reaction-limited process on growing surface of film. Also it is evident from the growth rate after t=180 min that as film becomes thicker UV transmission becomes less, causing decrease in growth rate.

CONCLUSION

We developed real-time spectroscopic ellipsometer to characterize the growth of polydiacetylene thin film using photo-assisted process. Photochemical cell and substrate were designed in such a way that ellipsometry spectra could be collected during the UV exposure. From the regression analysis using a single layer model, we found the low growth rate of 3 Å/min with 15 W mercury lamp and the reduction of growth rate as film became thicker. Moreover, we found that the growth process was greatly affected by the movement of solution indicating a reaction-limited process at solution-film boundary.

Acknowledgment
The authors wish to acknowledge the financial support of Hanyang University, Korea, made in the program year of 2000.

References

[1] Vedam, K., P. J. McMarr, and J. Narayan, *Appl. Phys. Lett.* **47**, 339 (1985)
[2] Vedam, K., *Thin Solid Films*, **313-314**, 1 (1998)
[3] Ord, J. L. and B. L. Wills, *Appl. Opt.* **6**, 1673 (1967)
[4] Collins, R. W. and S. Guha, J. *Non-Cryst. Solids* **77&78**, 1003 (1985)
[5] An, Ilsin, H. V. Nguyen, N. V. Nguyen, and R. W. Collins, *Phys. Rev. Lett.* **65**(18), 2274 (1990)
[6] Nguyen, H. V., Ilsin. An, R. W. Collins, *Phys. Rev.* **B 47**, 3947 (1993)
[7] An, Ilsin, H. V. Nguyen, N. V. Nguyen, and R. W. Collins, J. *Vac. Sci. Technol.* **A 9**(2), 632 (1991)
[8] Kim, Y. T., R. W. Collins, and K. Vedam, *Sur. Sci.* **233**, 341 (1990)
[9] Paley, M. S., D. O. Frazier, H. Abdeldeyem, S. Amstrong, and S. P. McManus, J. Am. *Chem. Soc.* **117**, 4775 (1995)
[10] An, Ilsin, Y. M. Li, H. V. Nguyen, and R. W. Collins, *Rev. Sci. Instrum.* **63**, 3842 (1992)