

CHEMICALLY DEPOSITED SILVER FILM USED AS A SERS-ACTIVE OVER-COATING LAYER FOR POLYMER FILM*

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Abstract When colloidal silver particles were chemically deposited onto polymer film as an over-coating layer, surface-enhanced Raman scattering (SERS) spectra could be collected for the surface analysis. SERS measurements of liquid crystal film were successfully performed without disturbing the surface morphology.

Keywords Surface enhanced Raman scattering, Chemically deposited silver, Polymer film

INTRODUCTION

When surface-enhanced Raman scattering (SERS) spectroscopy was discovered in 1970s, most of the research papers reported in the following years were devoted to gaining an understanding of the phenomenon itself^[1-3]. In 1990's there has been intense interest in the development of practically useful sample systems for the identification and characterization of adsorbed species. Practical silver substrate forms on which the SERS effect is observed most intensively include colloidal silver, silver island films on CaF_2 , silver films deposited on quartz or Teflon under vacuum^[4], and nitric acid etched silver substrate^[5]. Enhanced Raman scattering spectra could be easily collected from the samples adsorbed on SERS active substrates. SERS is now considered as one of the major techniques in the area of surface characterization. However, few experiments have been made on the surface of a fiber or a film by the SERS technique. Recently, we developed an effective SERS technique for characterizing the surface structure of film, without disturbing the morphology of the samples^[6]. The silver colloids were directly deposited onto the surface of film to form a SERS-active over-coating layer. The incident laser radiation penetrated through the silver over-coating layer and reached the surface of the samples. The scattered radiation, which contained the information about the film surface, was collected and then analyzed.

EXPERIMENTAL

All reagents were purchased from Aldrich Chemical Corp. and were reagent grade. The silver over-coating layer was prepared by depositing silver particle by the "Tollen's test" method onto the polymer film for investigation. A 10×10 nm piece of test film was placed in a 10 mL beaker and 5 mL 0.05 mol/L silver ammonia complex and 2 mL formaldehyde were mixed in the beaker. A few seconds later, the solution turned gray and black. Meanwhile the silver ions were reduced to form colloidal particles and were deposited onto the test film to form an over-coating layer at room temperature. The test film covered with silver over-coating was washed with

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distilled water and dried. Then the specimen was ready for Raman studies. The diameter of the deposited silver particles was a few tens of nanometers, measured by electron microscopy.

Raman spectra were mainly recorded with a Bruker IFS 100 Fourier Transform Raman Spectrometer equipped with an air-cooled Nd-YAG laser source (1064 nm), with an output power of 100~200 mW and a ultra-sensitive liquid nitrogen cooled Ge detector. The schematic diagram for back-scattering geometry is shown in Fig. 1.

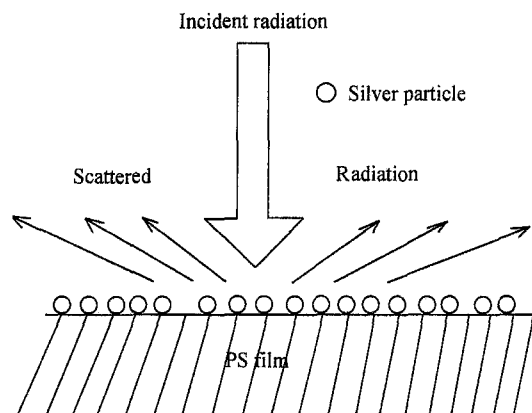


Fig. 1 Schematic diagram for back-scattering geometry for SERS measurement used in this paper

RESULTS AND DISCUSSION

Study on the Over-Coating Layer on Polystyrene Film

Two pieces of polystyrene film of 5 μm thickness were prepared by evaporating 3 wt% and 0.2 wt% solutions in benzene, respectively. Silver over-coating layers were deposited chemically onto these films. Laser radiation penetrated through the silver over-coating layer and interacted with the silver/polymer interface, the scattered radiation was collected from the silver over-coating layer. Figure 2 shows the SERS spectrum (Fig. 2a) collected from the silver over-coating layer on the polystyrene film prepared from 3 wt% solution, the spectrum (Fig. 2b) for the neat chemically deposited silver substrate and their difference spectrum (Fig. 2c), respectively. One can easily identify the vibrations associated with phenyl rings including the bands at 3055, 1603, 1032, and 1037 cm^{-1} , and the bands associated with backbone C-H stretching at 2902 and 2851 cm^{-1} . Figure 3 illustrates the corresponding spectra collected from the polystyrene film prepared from 0.2 wt% solution. Although the thickness of the film was the same as the sample in Fig. 2, the SERS spectra are quite different. In Fig. 3, the stretching band intensity of phenyl C-H at 3055 cm^{-1} and the ring stretching band at 1603 cm^{-1} are significantly reduced. However, the ring out-of-plane vibration at 760 cm^{-1} is enhanced, indicating that the benzene ring tends to lie flat on the surface. These spectral differences indicate that the molecular orientation at the surface for the film prepared from the dilute polystyrene solution is different from that prepared from concentrated solution. It seems that the chemically deposited over-coating silver can be used as a sensitive SERS technique for surface analysis of a film.

Study on the Rubbing Effect of a Liquid Crystal Film

Liquid crystal alignment, which is essential for liquid crystal display technology, is often realized by using rubbed polyimide films as alignment layer^[7]. Therefore, it is important for us to understand the mechanism responsible for this surface-induced liquid crystalline alignment, including the possibility of controlling the pretilt angle^[7]. This emphasizes the importance of knowing the molecular orientation and chemical structure of the polyimide surfaces. Most of the studies rely on bulk-sensitive methods such as infrared dichroism and optical retardation. Recently, some surface-sensitive measurements using electron spectroscopy for chemical analysis

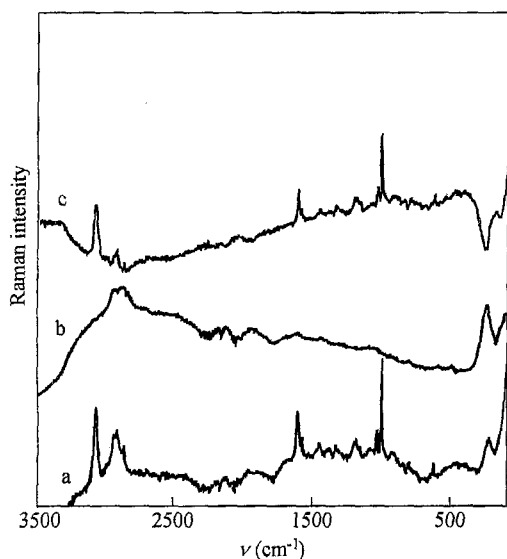


Fig. 2 (a) SERS spectrum of silver over-coating layer on polystyrene film prepared from 3 wt% solution; (b) SERS spectrum of a chemically deposited silver film; (c) Difference spectrum of A and B

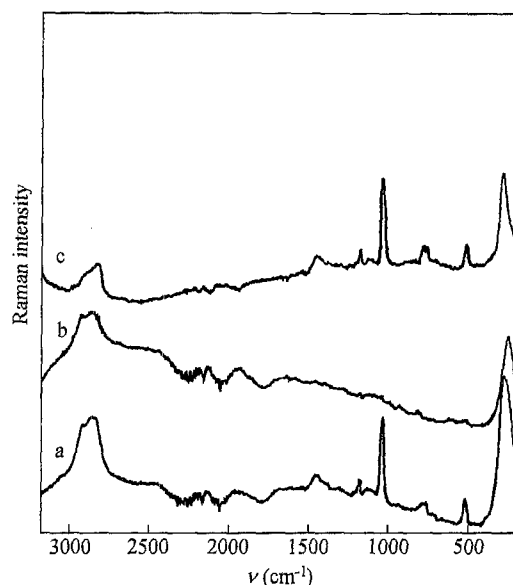


Fig. 3 (a) SERS spectrum of silver over-coating layer on polystyrene film prepared from 0.2 wt% solution; (b) SERS spectrum of a chemically deposited silver film; (c) Difference spectrum of A and B

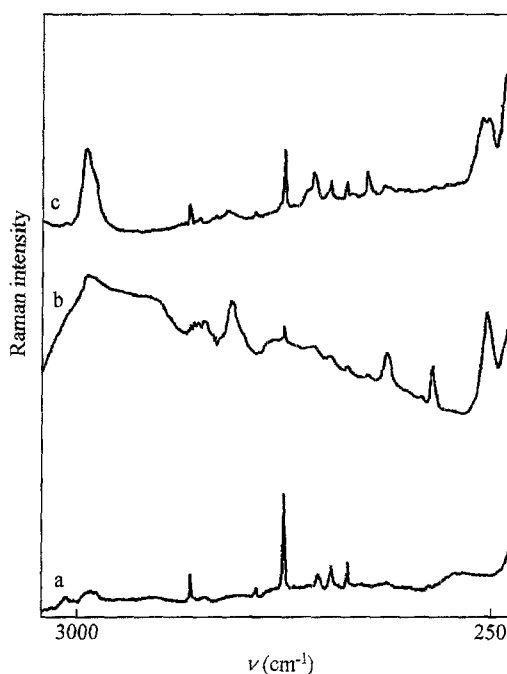


Fig. 4 (a) Normal Raman spectrum of a liquid crystal polyimide film; (b) SERS spectra for a silver over-coating layer on the non-rubbed polyimide liquid crystal film; (c) SERS spectrum for the silver over-coating layer on rubbed film

(ESCA) and X-ray scattering to obtain molecular orientation and structure of polyimide surface have been reported^[8-11]. A clear understanding of the correlation between the structure of polyimide surface and bulk liquid

crystal alignment is still lacking, suggesting the need to use some other surface sensitive experimental techniques. In this paper, we report the study of a polyimide, which has a cyano group in the side chain, specially designed for high pretilt liquid crystal alignment with SERS. Thin polyimide film for SERS measurements was made by spin-coating 2 wt% solution in cyclopentane onto a glass substrate followed by baking at 120°C for 20 h. The thickness of the film was controlled to 3~5 μm . Rubbing of the film was carried out on a rotating drum wrapped with velvet. The silver colloid was directly deposited onto the rubbed and the non-rubbed surface of the polyimide films simultaneously. Figure 4(a) shows a normal Raman spectrum of the polyimide film, which shows characteristic bands for cyano group at 2227 cm^{-1} and for aromatic ring at 1606 cm^{-1} . Figures 4(b), and 4(c) illustrate the SERS spectra for a non-rubbed polyimide liquid crystal film and the rubbed film, respectively. The SERS spectrum (Fig. 4b) of the non-rubbed film is quite different from that of the bulk film in the intensity of the 2229 cm^{-1} , 1606 cm^{-1} , 920 cm^{-1} and 610 cm^{-1} bands. It indicates that the molecular alignments at the polyimide surface are different from those in the bulk. In the spectrum of the rubbed film (Fig. 4c), although their relative intensities are different because of the selection rules associated with surface enhancement on metals, the 2229 and 1606 cm^{-1} bands are seen clearly in the SERS spectrum. Therefore, we can presume that the surface structure of the polyimide film is different before and after rubbing, indicating that the rubbing process can significantly rearrange the surface orientation distribution of the side-chains, and slightly changes the alignment of the backbone. This result may shed some light on the understanding of the molecular mechanism responsible for aligning liquid crystal by rubbed polyimide and the systematic design of alignment layers for inducing high-pretilt liquid crystal bulk alignment.

CONCLUSIONS

In this communication we have evaluated the use and performance of a simple and inexpensive silver over-coating system for Raman studies, which could significantly increase the applicability of the SERS technique. Since the coating process was performed in water and at room temperature, most organic polymer films and fibers were stable under these conditions, and the surface morphology would not be disturbed. We have also performed SERS measurements with the chemically deposited silver over-coating layer on samples of current interest, such as nanometer diameter fibers and liquid crystals. The results of this work show that our SERS sampling technique is particularly effective.

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