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Thin Film Formation of 2-Methyl-4-nitroaniline by Ionized Cluster Beam Technique

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Thin films of 2-methyl-4-nitroaniline were prepared by an ionized cluster beam (ICB) technique. Their SEM photographs suggested that the ICB-deposited films are much denser than vacuum-deposited films. X-Ray diffraction patterns suggested that the control of a preferential orientation is possible by changing the substrate temperature.

Ionized cluster beam (ICB) deposition[1] has been attracting much interest as a useful method for preparing organic films which have preferential orientation and high crystallinity. Several kinds of organic materials have been deposited by this method.[2,3] In preparing integrated electrical or optical devices of functional organic materials, it is necessary to control the crystallinity and orientation of the thin films which are made of such materials. We examined the thin film formation by ICB deposition of 2-methyl-4-nitroaniline (MNA), a well known organic, nonlinear optical material[4] and evaluated its structural properties.

Figure 1 shows a schematic diagram of the apparatus used for the ICB deposition. The source material was MNA purified by sublimation. A crucible made of highly-purified graphite with a cylindrical nozzle (1 mm diameter and 1 mm long) was used. Attempts to keep the crucible at a constant temperature just below the melting point of MNA, 131 °C, failed owing to the heat generated by the ionization filament. The deposition began when the temperature of the crucible reached 85 °C and was completed when it reached ca. 120 °C. The electron acceleration

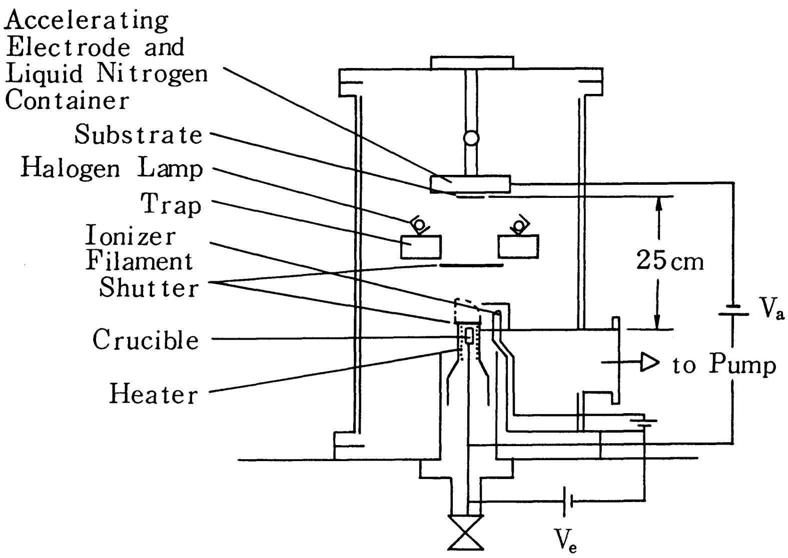

Fig.1. Schematic diagram of the ICB deposition apparatus.

voltage for ionization, V_e, was fixed at 300 V and the electron current for ionization, I_e, was varied from 0 A to 8 mA. The acceleration voltage of cluster ions, V_a, was varied from 0 V to 500 V. Commercially available glass slides were used as substrate. The substrate temperature, T_s, was changed from -80 °C to 0 °C. At temperatures higher than 0 °C, MNA could not be deposited. Vacuum deposition was done using this apparatus, too, with a background pressure during the deposition , about 1.3 mPa.

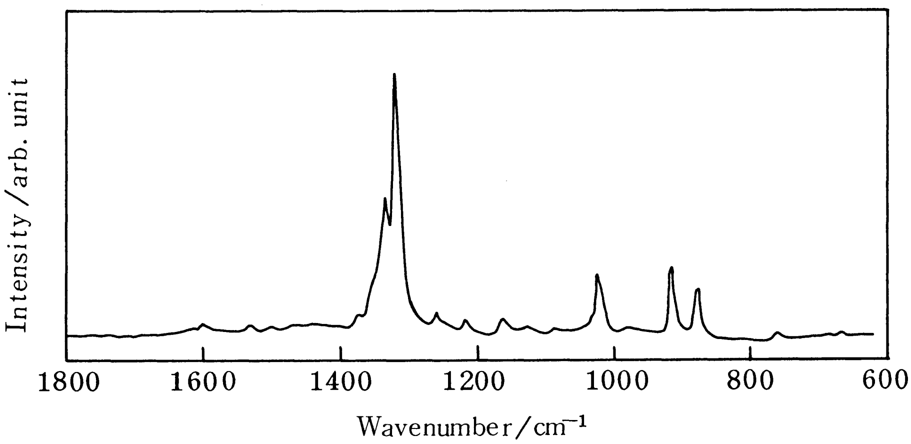

Fig.2. Raman spectrum of an MNA thin film deposited by ICB technique. (V_a= 500 V, I_e= 8 mA and T_s= -80 °C; Wavelength of light for excitation: 514.5 nm)

MNA was deposited without being decomposed during the ICB process, as indicated by the Raman spectrum of a thin film obtained by this procedure (Fig.2), which shows peak frequencies almost the same as those reported by Szostak.[5)]

Figure 3 shows SEM photographs of the thin films that were prepared with four different procedures: (1) vacuum deposition, (2) cluster beam deposition (I_e= 0)(deposition of neutral clusters), (3) ICB deposition (I_e= 5.5 mA) and (4) ICB deposition (I_e= 8 mA), the substrate temperature being -80 °C. In (3) and (4), V_a was fixed at 500 V and the film thickness of these films was about 1.0 μm. The film prepared by the vacuum deposition consisted of needle-shaped crystals and was very porous. The film prepared by the clus-

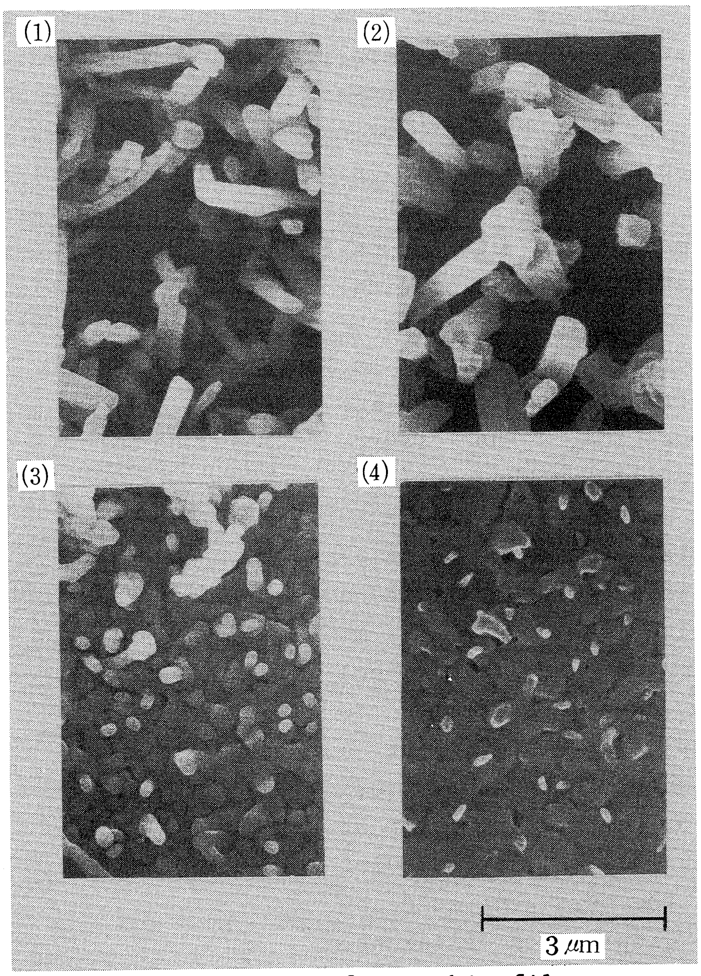

Fig.3. SEM photographs of MNA thin films prepared by (1) vacuum deposition, (2) cluster beam deposition, (3) ICB deposition(I_e= 5.5 mA) and (4) ICB deposition(I_e= 8 mA).

ter beam deposition had the same features. In contradistinction to these films , the film deposited by the ICB technique did not contain needle-shaped crystals and it was much denser. It is considered that this difference in the microscopic appearance was caused by the ionization of cluster.

Figure 4 shows the X-ray diffraction patterns of the thin films deposited by different techniques. Though the film thickness was the same, the diffracted X-ray intensity of the ($\bar{3}$11) diffraction peak of the film deposited by the ICB technique was much higher than the others. This fact indicates that the ICB-deposited film had much higher crystallinity. Furthermore, this film had a preferential orientation, as diffractions other than ($\bar{3}$11) peak were virtually absent.

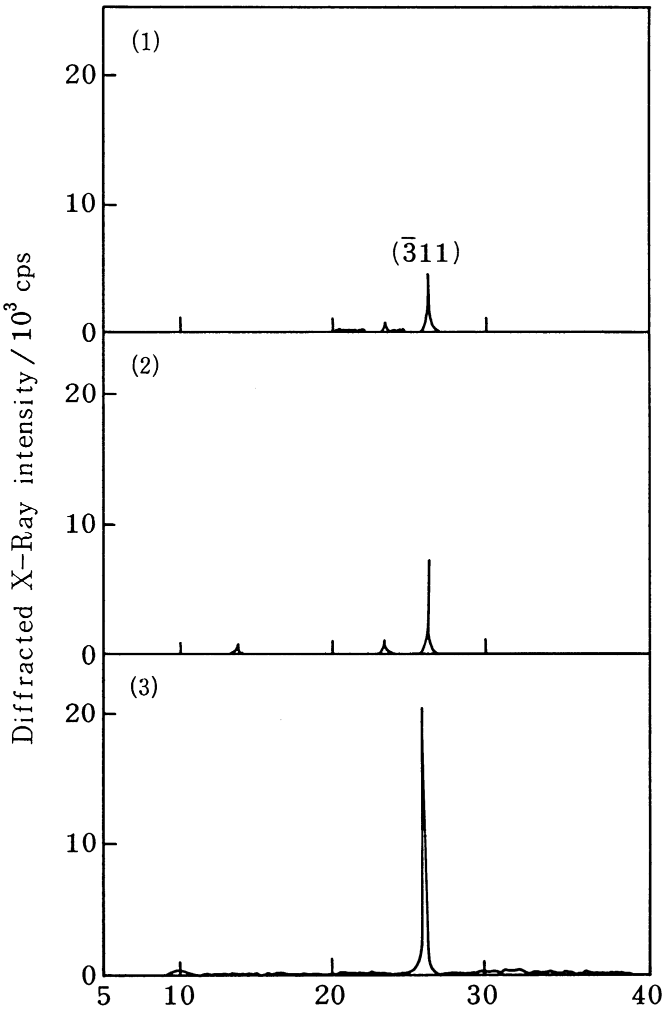

Fig.4. X-Ray diffraction patterns of MNA thin films prepared by (1) vacuum deposition, (2) cluster beam deposition, and (3) ICB deposition (I_e= 8 mA).(CuKα)

Figure 5 shows X-Ray diffraction pattern of ICB deposited films at different T_s. When T_s= 0 °C, ($\bar{3}$11) and (020) peaks were apparent and the ratio of (020) to ($\bar{3}$11) peak heights was appreciably higher than that in diffraction pattern of MNA powder. Powder is a non-preferential assembly of microcrystals. Consequently, this fact indicates that this film contained more microcrystals of which (020) planes are parallel to the substrate surface than those of which ($\bar{3}$11) planes are parallel to the substrate surface. This feature is similar to that of the result reported by Dohmoto et al.[6)] However, when T_s was lower than -30 °C, (020) peak was almost non-apparent and ($\bar{3}$11) peak was only apparent virtually. Consequently, most of microcrystals of this film have ($\bar{3}$11) planes parallel to the substrate surface. It appears that the direction of the orientation changed as the substrate temperature became higher. In order to use polycrystalline thin films for second harmonic generation, it is preferable that the polar axis of MNA crystalline is normal to the substrate. The polar axis is parallel to (020) and ($\bar{3}$11) planes. Thus films that we obtained at this time are not useful. We consider that this problem may be solved by using different substrates.

In conclusion, we confirmed the ICB deposition is useful as a means for preparing thin films of MNA that have high crystallinity, preferential orientation, and high density and the direction of orientation can be controlled by changing the substrate temperature.

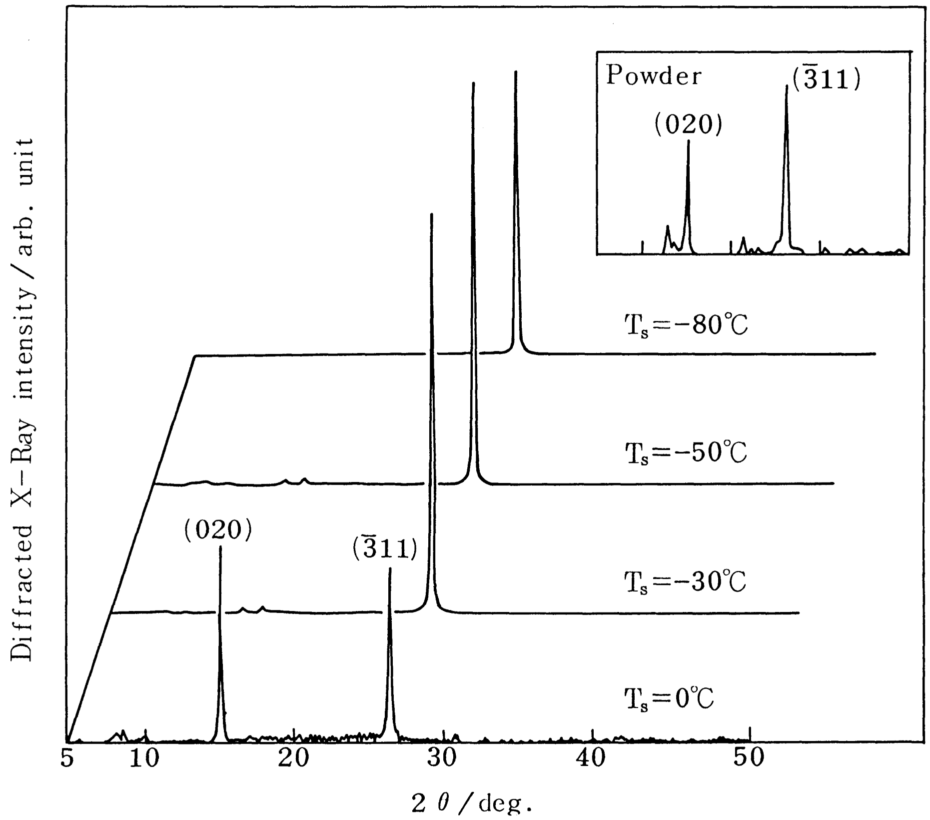

Fig.5. X-Ray diffraction patterns of MNA thin films deposited at different substrate temperature. (V_a= 500 V, I_e= 8 mA)(CuKα)

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