Photo-thermally Induced Phase Transition in Vanadyl Phthalocyanine Thin Film

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A vanadyl phthalocyanine (VOPc) film (Phase I) on a mica substrate was prepared and photoinduced phase transition of VOPc was tried. Changes in absorption spectra show that Phase I structure is converted to Phase II structure by the irradiation with He-Ne laser. The surface structural changes of VOPc were also observed by using atomic force microscopy (AFM). Experimental results suggest that the phase transition was induced by photo-thermal processes.

Metallo-phthalocyanines have attracted much interest for possible applications in molecular devices in various fields because of their chemical and thermal stability and wide capability to synthetic modification.[1-5] One of the unique properties of metallo-phthalocyanines is crystal polymorphism. In general, various metallo-phthalocyanines have been shown to exist in at least three polymorphic modifications (α, β and χ).[6] Vanadyl phthalocyacnine (VOPc) is especially of interest for opto-electronic applications because the properties of VOPc strongly depend on the molecular stacking structure of the thin film or crystal. VOPc crystals have been shown to exist in three polymorphic modifications (Phase I, II and III) and their properties have been characterized by the absorption spectra and X-ray diffraction analyses.[7] Among these modifications, Phase III is the most stable state thermodynamically. Phase I and II are meta-stable states.[8] Thus, it is expected that phase transition between these phases could be induced by purely optically or photo-thermally.

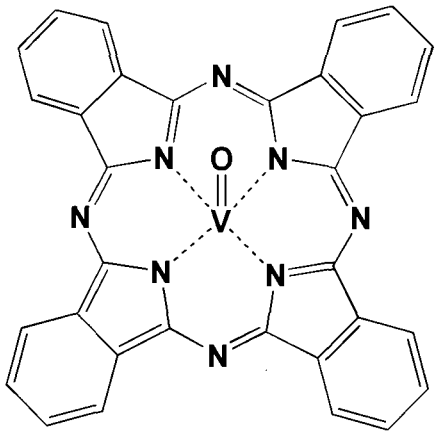

Figure 1. Chemical structure of vanadyl phthalocyanine (VOPc).

In this work a VOPc film (Phase I) was prepared on a mica substrate and photoinduced changes in the film and on the surface were monitored by absorption spectroscopy and atomic force microscopy (AFM), respectively.

VOPc films were prepared by the vapor deposition using a commercial system (ULVAC, Model VPC-410) as follows. A 2.0 mg sample of VOPc powder, which was purified by vacuum sublimation, was evaporated onto a mica substrate from a quartz

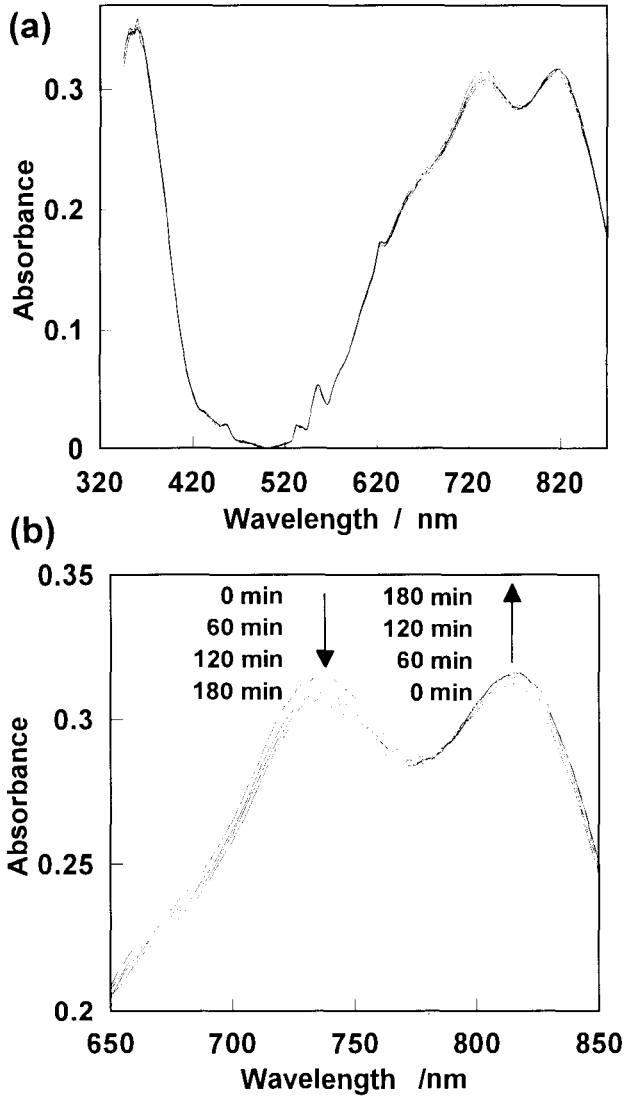

Figure 2. Absorption spectral changes of VOPc film with iradiation time (incident laser light : 633 nm). (a) change of region between 320 and 850 nm, (b) change of region between 650 and 850 nm (Q-band).

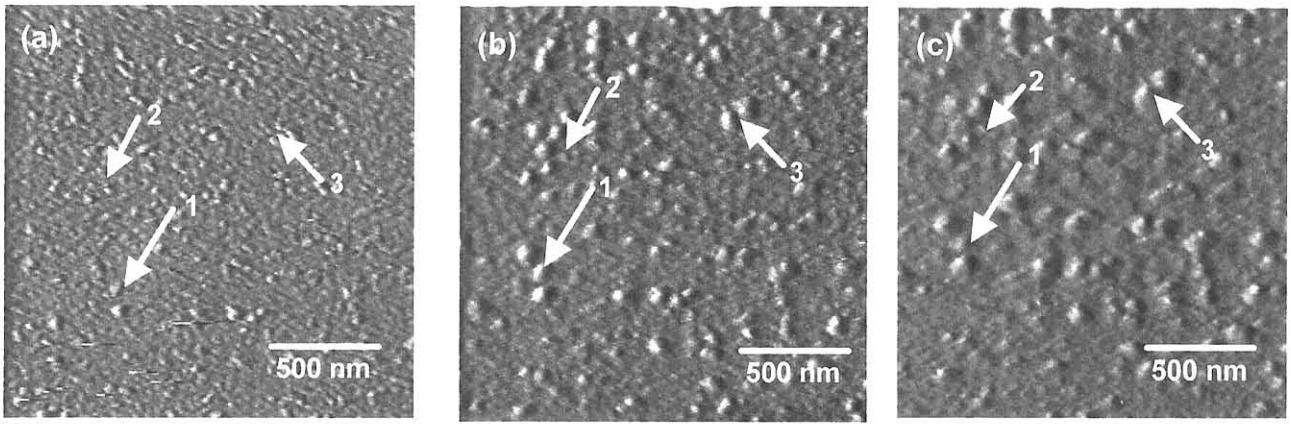

Figure 3. Surface changes of VOPc film by irradiation with 630 nm light. (a): Before irradiation (b): After irradiation for 1 h (c): After irradiation for 2 h.

crucible resistibly heated by a tungsten boat under a vacuum of 10^{-6} Torr. The mica substrate was kept at 25 °C and the deposition rate was controlled at 1.0 nm s^{-1} by monitoring it with a quartz-crystal microbalance (QCM). The thickness of the VOPc film was controlled to 50 nm. Changes in the absorption spectrum of the VOPc film were measured using a Shimadzu spectrometer (Model UV-3100). A He-Ne laser (633 nm, 20 mW) was used as the excitation light source. The light intensity was fixed at 1.0 W cm^{-2} by focusing the light to be 1.0 mm. AFM measurements were carried out using a commercial system (Seiko Instruments Inc., Model SPI 3700), and commercially available triangular shaped Si_3N_4 cantilevers under ambient atmospheric conditions.

From the absorption spectrum, the as-prepared VOPc film was assigned to the Phase I polymorphic modification.[7] Upon the irradiation with 633 nm light, the absorption spectrum changed as shown in Figure 2. No changes in the Soret band at 350 nm were observed, however, the Q-bands at 725 and 825 nm changed with the irradiation time. The absorption bands at 725 and 825 nm decreased and increased with the irradiation time, respectively. After the irradiation the absorption spectrum turned to that of Phase II,[7] indicating a transformation from Phase I to II induced by the irradiation. By using molar coefficient extinction of Phase II,[7] the transformation of Phase I to Phase II was estimated to be 52% with irradiation for 180 min. Similar spectral change was also observed upon irradiation with 514 nm light (ε ~200 mol^{-1} dm^3 cm^{-1} at 514 nm), showing this transformation was independent of the excitation wavelength. Phase II is more stable state than Phase I thermodynamically.[8] Thus, this transformation was considered to be due to a photo-thermal effect of laser irradiation.

The surface structural change by the laser irradiation was observed by AFM. Figures 3 (a), (b) and (c) are images of the same area (as indicated by arrows). Figure 3 (a) shows the image of the surface of the VOPc film before laser irradiation. After laser irradiation for 1 hour, the crystalline islands of VOPc changed as shown in Figure 3 (b). In Figures 3(a) and (b), the islands of VOPc were enlarged by laser irradiation. After further irradiation (1 hour), the islands expanded as shown in Figure 3 (c). These expansions were induced by a transformation from Phase I to II or growth of crystalline by the photo-thermal effect. The intermolecular distances in the *c*-axis direction became longer by the transition from Phase I to II (the distance of Phase I and Phase II are 0.78 nm and 0.88 nm, respectively).[7] Thus, it is concluded that these crystalline island expansions were induced by a phase transformation.

In summary, we have shown that phase transition from Phase I to II occurred on the VOPc film by the irradiation. This transformation was independent of the excitation wavelength, indicating that the phase transition was induced by photo-thermal processes. Further investigation will provide the reversible phase transition between these phases induced by purely optically and photo-thermally.

Reference and Notes

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