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OBSERVATION OF GENERATION OF INTENSE SECOND-HARMONICS AT ETCH PITS OF *p*-NITROANILINE SINGLE CRYSTAL SURFACE

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Abstract We found that bright green spots could be observed with eye when the cleaved surface of a *p*-NA single crystal, which had been stored for a few weeks after cleavage, was irradiated with a 1.06 μ m pulse, an observation which indicates that strong SHG occurred on the crystal surface. The bright spots corresponded to etch pits developed as a result of slow evaporation. Growth of a new phase having an acentrosymmetric structure is probable.

INTRODUCTION

Second-harmonic generation (SHG) at surface or interface has become a powerful tool for investigating molecular orientation at these phase boundaries. It is a nonlinear variant of polarization spectroscopy, but it can be highly surface-sensitive, due to the lower symmetry of the surface. In a previous publication we reported a SHG study of freshly cleaved surface of a single crystal of *p*-nitroaniline. The results indicate that the surface has the same symmetry with that expected from the bulk structure [1].

p-Nitroaniline (*p*-NA) has a large second-order polarizability β . However, it crystallizes into a centrosymmetric structure due to their strong dipole-dipole interaction and the crystal is generally considered to be inactive in SHG. We observed that, just after cleavage, the surface was smooth when viewed under microscope, and weak but finite second-harmonics could be detected [2]. In the course of 2-3 weeks the surface became rough under microscope. When the surface was scanned with a tightly focused beam of a pulsed laser, there was a strong variation of the SH intensity over the rough surface. Here will be reported an observation of the surface with SHG-detected microscopy and with conventional photomicroscopy.

SAMPLE PREPARATION AND SH-DETECTED MICROSCOPY

p-NA was purchased from Tokyo Kasei Co. and was zone-refined. Single crystals were grown from the melt by the Bridgman method.

An experimental arrangement for SH-detected microscopy is shown in Fig.1. The surface of a *p*-NA crystal was illuminated with a softly focused beam from a Q-switched Nd:YAG laser (100 μ m diam.), while SHG is monitored. We could take a picture of the surface with SH detection with an exposure of a single laser shot. The energy of the laser pulse was reduced to 0.5 mJ / pulse to avoid damage of the surface. The lens (L) was fixed on a two-axis translator which was driven by stepping motors, controlled by a computer. The cleaved surface was (101) plane. The SH intensity was the largest, when the fundamental was incident normal to the surface. We used objective lens (L1) of magnification 10. The fundamental and SH components were separated with dichroic mirrors. The SH intensity at the surface was in the same order of that from quartz.

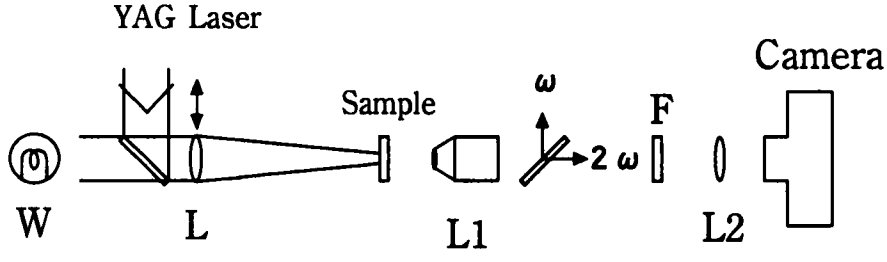

FIGURE 1 Experimental arrangement for SH-detected microscopy.

RESULTS AND DISCUSSION

We observed that many etch pits developed on the surface of a *p*-NA crystal during 1-2 weeks after its cleavage. We believe that this formation of pits is the result of slow evaporation of the surface molecules at dislocations at room temperature (thermal etching). Figure 2(a) shows a photograph of the etch pits. An image of the same area taken with SH is shown in Fig.2(b). The bright spots correspond to etch

pits. The SH signal from the bright spots is polarized, just as the signal from a smooth area.

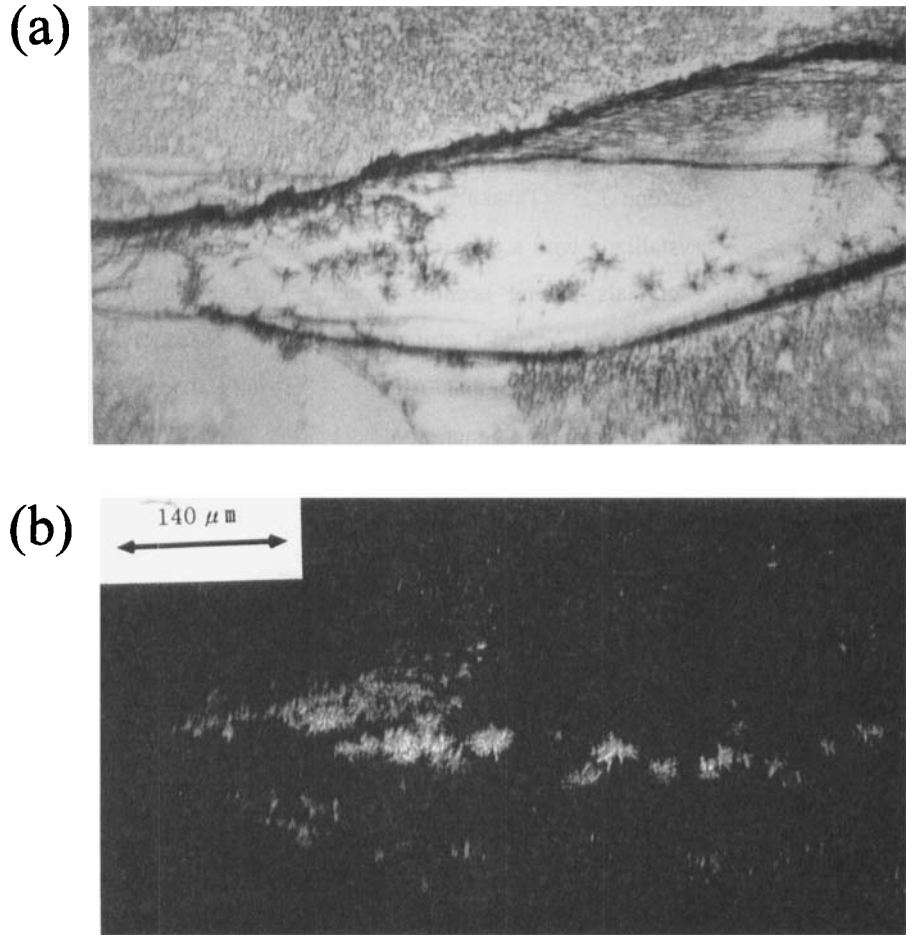

FIGURE 2 Photographs of (a) etch pits developed as a result of slow evaporation and (b) image of a crystal surface taken with SH. Bright green spots coincide with etch pits. The SH signal is strongly polarized. See Color Plate I.

A parallel experiment was made in which a freshly cleaved crystal was kept in a vacuum (10^{-3} Torr) for several hours. Many etch pits, 1-100 μ m in dimension, developed on the surface. Figure 3 shows a microscope picture of such surface. A row of etch pits is clearly seen which indicates that they are aligned along a slip

plane. At these etch pits which developed in a relatively short time the SH intensity was quite low. This seems to indicate that the formation of etch pits is not sufficient for the SHG. It is probable that at etch pits where intense SH was observed tiny crystals formed which have a SH-active structure. Actually there are reports on the growth of a SHG-active phase of *p*-NA. Miyazaki et al. observed that *p*-NA crystallizes spontaneously in a non-centrosymmetric structure in guest-host mixture with poly (ε -caprolactone) [3]. Tasaka et al. reported SHG-active *p*-NA crystals formed when *p*-NA crystallized with a derivative of *p*-NA [4]. Kamio et al. observed the growth of *p*-NA crystals having acentrosymmetric structure by quenching a melted mixture of poly (γ -benzyl-L-glutamate) and *p*-NA down to room temperature [5]. Cox et al. reported that $AlPO_4$-5 crystals loaded with *p*-NA exhibit strong optical second-harmonic generation [6].

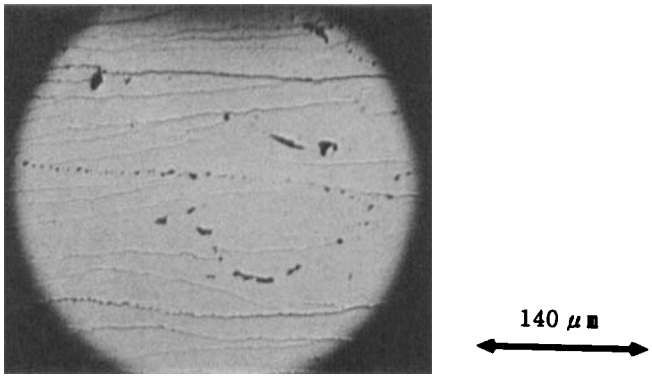

FIGURE 3 Photograph of etch pits developed when the crystal was kept in a vacuum. A row of etch pits is clearly seen which is clearly seen which indicates that they aligned along a slip plane. See Color Plate II.

A similar observation was made when *p*-NA was deposited, by vacuum sublimation, onto a cleaved surface of a single crystal of *p*-cyanoaniline (*p*-CA). We reported an observation of the growth of a well oriented layer of *p*-NA onto the surface of *p*-CA [7]. The structure of *p*-CA as well as *p*-NA has an inversion symmetry and

SHG from the bulk of the crystal is forbidden. The SHG at the surface of a *p*-CA crystal is much weaker than that at a *p*-CA surface covered with a *p*-NA layer, so that we can regard the SH signal observed to be due to the deposited *p*-NA layer. *p*-CA has a fairly high vapour pressure and accordingly many etch pits developed on the substrate when a *p*-CA crystal was kept in a vacuum (5×10^{-5} Torr). Figure 4(a) shows the photograph of a deposited *p*-NA film on a *p*-CA single crystal, and fig.4(b) shows the image of the film taken with SH detection. The bright spots correspond to the etch pits. It is probable that a SHG-active crystal of *p*-NA grow at etch pits of the substrate. The SH signal is strongly polarized parallel to the *c* axis when the polarization of the fundamental is parallel to the *c* axis of the substrate. When the polarization of the fundamental is parallel to the *b* axis of the substrate, the SH signal is much weaker. These observations imply that *p*-NA molecules deposited at etch pits of the substrate are well oriented to the crystal lattice of the substrate.

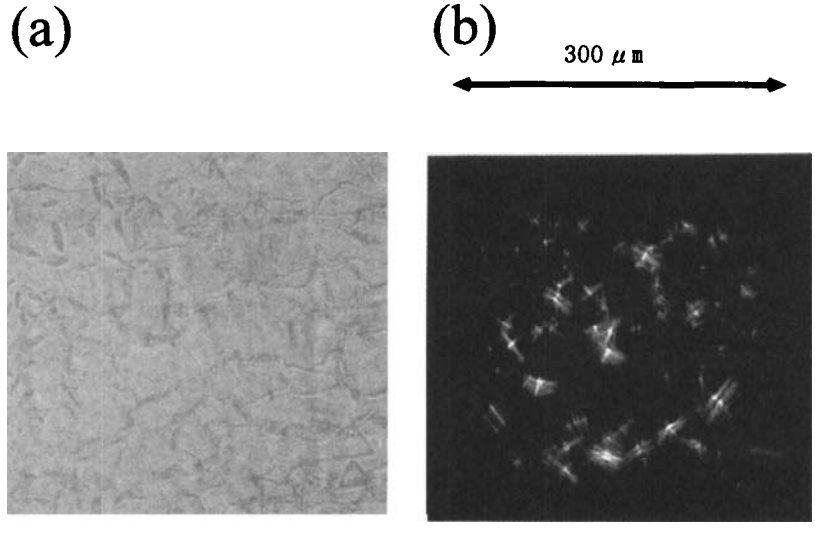

FIGURE 4 Photograph of *p*-NA film deposited on a *p*-CA single crystal (a) with conventional lighting, (b) the same field taken with SH detection. The SH signal is strongly polarized parallel to the *c* axis when the polarization of the fundamental is parallel to the *c* axis of the substrate. See Color Plate III.

In summarizing we observed generation of intense second-harmonics at etch pits on a *p*-NA single crystal and in a well oriented layer of *p*-NA deposited on the surface of *p*-CA. The bright spots correspond to etch pits. It is probable that tiny crystals having an acentrosymmetric structure which grow at etch pits are responsible for strong SHG. SHG can be a sensitive method for studying orientation of molecules at surfaces when the bulk structure is centrosymmetric.

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