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Color Change Due to Phase Transition in N-(2,4-Dinitrophenyl)-*o*-Anisidine

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N-(2,4-dinitrophenyl)-*o*-anisidine changes its color from orange to red with change in crystal structures. The orange phase transforms irreversibly into red phase by heating In the present study, we observed the transformation process by atomic force microscopy to make clear the microscopic transition mechanism. The observed images revealed that the red phase is resulted by sublimation of molecules from orange crystal by changing its conformation to the red one and re-adherence to the orange surface with epitaxial relation.

Keywords: N-(2,4dinitrophenyl)-*o*-anisidine; phase transition; atomic force microscopy; epitaxy

INTRODUCTION

Recently Iwasaki *et al.* have reported that N-(2,4-dinitrophenyl)-*o*-anisidine (N-DNPA) (FIGURE 1) change irreversibly its color from orange to red in solid state by heat treatment corresponding to two crystal structures; the orange and the red phases [1]. The condition of transformation is, however, very subtle, and both phases often coexist. The boundary area of both phases as well as each pure phase have already been studied by X-ray diffraction analysis [1], which has given the crystallographic relation between two phases. However, the microscopic mechanism of the

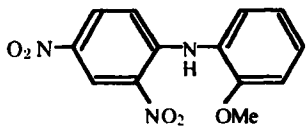

FIGURE 1 Chemical formula of N-DNPA.

phase transition has still not been solved, and therefore we examined the relationship between the two phases by observing the boundary region with an atomic force microscope (AFM). The transition mechanism will be discussed from the present result and the previously reported X-ray data.

EXPERIMENTAL

According to the previous X-ray results [1], the crystal systems in both phases are monoclinic, and the molecules in each phase take rotational isomers. During the transition, the directions of the b-axes of both phases coincide each other so that the whole molecules have to rotate by about 90° as shown in FIGURE 2, but the direction of the a- and c-axes of both phases do not correspond simply.

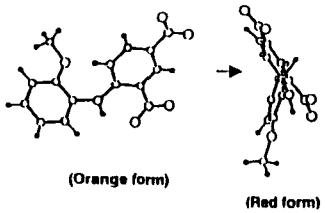

FIGURE 2 Projected molecules along the b-axes in orange and red phases.

By careful heat treatment, we prepared a needle-like single crystal in which the both phases coexist; the half of the crystal has turned into the red. From X-ray, the b-axes of both phases align along the needle axis of the crystal. The AFM measurement was carried out at room temperature with a Nanoscope IIIa in contact mode. The surface of both phases and their boundary area were examined.

RESULTS AND DISCUSSION

An AFM image shown in FIGURE 3 exhibits a boundary area between the two phases. The direction of b-axes of both phases is shown by the arrow in the figure. The orange phase is observed in upper left-handed part of the image and retains flat single crystalline surface, while the red phase, in the right part, consists of the small grains. The observed red crystals grew in various directions so that we can conclude this transformation as a non-topochemical. In the boundary area, two important features are observed.

The first is that, in the red part, some dot-like contrasts are continued along the b-axis, which seems to correspond to the step edges in the orange surface. Accordingly, the crystal growth of the red phase should be affected by orange phase surface. The second is that triangular hollows are observed in the orange side at the boundary indicated by the white arrows. One of the triangle edges is vertical to the b-axis; the (010)-plane of the orange phase, and the other one is parallel to the b-axis. The triangular hollows suggest that the red phase formation would be due to sublimation from this area, followed by adhesion (or growth) onto the orange surface.

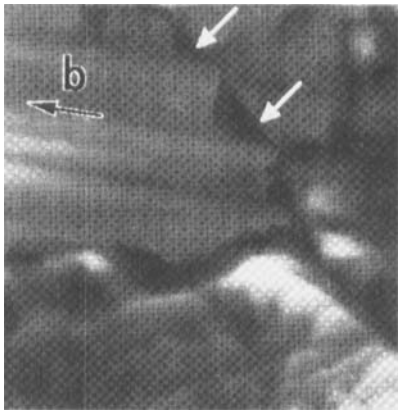

FIGURE 3 An AFM image at a boundary between the orange and the red phases (15μm×15μm).

The mechanism of this phase transition can be illustrated as the followings: Firstly, the conformation on the (010)-plane of the orange phase changes by heating, which is clearly related with the higher thermal expansion along the b-axis. Secondly, the red phase molecules sublimate and re-adhere onto a surface of the orange phase so as for their molecular planes to be parallel to the orange surface. Finally, the red phase crystals grow epitaxially on the orange phase substrate. Here, the orange substrate surfaces might be lower indexed planes such as (001), (110) or ($10\bar{1}$), because these planes are likely to form the outer surface of the crystal. The crystallographic relation between both phases revealed by X-ray analysis can be explained from this model. From X-ray measurements, the orientation of the a- and c-axes of both phases do not correspond uniquely, but the axial relations between the two phases have been summarized as in the following three cases; the a-axis of the red is (i) parallel to the a-axis of the orange, (ii) parallel to the c-axis of the orange, or (iii) perpendicular to the a-axis of the

orange. When the direction of the both b-axes are common, these orientation relations can be expressed in another way as the $(30\bar{1})$ of the red phase is nearly parallel (i) to the $(10\bar{1})$, (ii) to the (110) or (iii) to the (001) of the orange phase, respectively.

Based on the mechanism of the phase transition described above, the molecular plane in the red is expected to be parallel to one of the low-index planes of the orange as shown in FIGURE 4. In the red phase the molecules align almost parallel to the $(30\bar{1})$-plane, even though the molecule is not completely plate-like. As a result, the $(30\bar{1})$-plane of the red-phase becomes parallel to the (001), (110) or $(10\bar{1})$, which is consistent with the result of X-ray measurements.

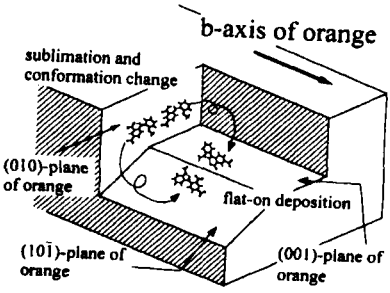

FIGURE 4 Schematic drawing of the transition through gaseous epitaxial growth.

In order to explain the b-axis orientation of the red phase, epitaxial growth mechanism of the red phase on the orange phase is plausible. The lattice misfit along the b-axis is estimated as 4.6% between the (050)-plane on $(30\bar{1})$-plane of the red and the (001)-plane of the orange. This value is the smallest as far as we consider the lattice matching between the $(30\bar{1})$ of the red and low indexed planes of the orange, so that the b-axes of both phases align parallel.

The phase transition from the orange phase of N-DNPA is concluded as a gaseous epitaxial growth onto the orange phase. It can also be confirmed from the fact that the transformation hardly happens under vacuum.

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References

[1] M. Yasui, K. Taguchi and F. Iwasaki, *Mol. Cryst. Liq. Cryst.*, **277**, 167-176(1996).