The conductivity of a silver salt of N,N’-dicyanoquinonediimine irreversibly varied in approximate proportion to an illumination of a wide range of wavelengths. Depending on the illumination conditions, four different states (β, γ, δ, and ε) were obtained with different structures. The
β structure is in particular important, where the formal charge of the N,N’-dicyanoquinonediimine molecules continuously decreased to -0.4 – -0.35 with retaining the crystal structure, when we kept the temperature < 155°C during the illumination. The non-illuminated area of the sample retained its original electrical property with a well-defined interface, which enabled a fabrication of a junction-structure in the single crystal.

Keywords: photo-induced phenomena; molecular semiconductor-metal junction; N,N’-dicyanoquinonediimine; charge-transfer; doping

INTRODUCTION

Recently we reported on a new method of persistent electrical resistivity control of the molecular materials containing photosensitive chemical species [1]. At present, the chemistry of this method is considered to be approximately similar to the silver halides photography. A silver salt of an organic π−acceptor molecular radical anion, Ag(DM)₂ (DM = 2,5-dimethyl-N,N’-dicyanoquinonediimine; Fig. 1), is utilized instead of silver bromide. In the crystal of Ag(DM)₂, the planar radical-anion species of DM stack to form a columnar structure [2]. The unpaired electrons on the radical-anion species delocalize along these columns, resulting in metallic conduction. Similar to AgBr, exposure to ultraviolet-visible (UV-Vis) light of Ag(DM)₂ leads to a partial charge transfer from the π−acceptor molecules to the silver ions in the solid state. This charge transfer corresponds to decrease of the π−electrons in number on the DM radical-anion
species. Because the electrical conductivity is solely dependent on the $\pi$-electrons on the DM radical-anion species in Ag(DM)$_2$, such charge transfer results in the decrease of conductivity of this material. What is more, illumination on a limited part of the sample resulted in the change in conduction only at the illuminated part; the rest of the sample retained the original metallic conduction. Such a scenario is supported by X-ray photoelectron spectra (XPS) (Ag, N), and Raman spectra (C=C and C=N stretching modes) [1]. In combination with photolithography or light-focusing techniques, these findings might open a new way to control electrical properties of a particular part of a molecular solid, which would lead to fabrication of devices with junction-structures. In fact, using this method we demonstrated that one could produce an energy barrier in a single crystal of Ag(DM)$_2$, which indeed exhibited rectifying behavior; i.e., characteristic behavior to diodes [1]. In addition to the partial charge transfer semiconductor phase, we have found several phases created according to the illumination time and power. Therefore we must understand the properties and structures of these new phases and their formation mechanism in order to establish and develop this method to control electrical conductivities with as high spatial resolution as possible. In this brief communication we investigated the heat effects and wavelength dependence in addition to the characterization of several phases.

**EXPERIMENTAL**

We used two light sources depending on the experiment. One (light source A) was a UV-VIS FIBER LIGHT SOURCE L7893 equipped with a 5 W-tungsten halogen lamp (400-1100 nm) and a 30 W-D$_2$ lamp (200-400 nm), and with optical fiber of 800 $\mu$m in core diameter (numerical aperture = 0.22) (HAMAMATSU PHOTONICS K. K.). Both
of the lamps could be turned on/off independently, but the power of light could not be varied. The end of the fiber was placed as close to the surface as possible (< 150 μm). The output of the incident beam at the end of the fiber is typically 0.1-0.2 μW cm\(^{-2}\) nm\(^{-1}\) at 300-550 nm, 0.2-1 μW cm\(^{-2}\) nm\(^{-1}\) at 200-300 and 550-1100 nm. In a typical run we used both of the 5 W-tungsten halogen and the 30 W-D\(_2\) lamps, when the power was ~ 3 mW at the end of the fiber. The typical value of the fluctuation of the output during continuous illumination is 0.004 % and the drift 0.3 %h\(^{-1}\). The other (light source B) was a Hg/Xe lamp (200 W; HAMAMATSU PHOTONICS K. K.) with a multimode optical fiber (1m-length, φ = 5mm, numerical aperture = 0.22) (SUPERCURE-203S UV LIGHTSOURCE; SAN-EI ELECTRIC). This light source was also equipped with a removable filter and an aluminum mirror for cutting off the light with wavelengths shorter than ~250 nm and longer than ~ 800 nm, respectively. This could minimize heat involved in the irradiation of the sample. The power of light of this light source could be varied continuously up to ~300 mW at the end of the fiber. The maximum power depended on the wavelength. When UV light of 200-250 nm was required, the filter was removed. During the illumination with the light source B, the sample was set in a copper or brass stage as a heat reservoir, and the temperature was continuously monitored. An anomalous deviation (> 0.1 K) from the room temperature (RT) then was not observed.

**RESULTS AND DISCUSSION**

**Optically “Doped” States without Heating Effects**

We obtained four different kinds of resultant states depending on the illumination conditions as shown in Table 1. Including the pristine material, let us tentatively call
these series of states $\alpha$, $\beta$, $\gamma$, $\delta$ and $\epsilon$, respectively. All the states should involve charge transfer (redox) reaction between the Ag ions and the DM species based on their characterizations. As for the production of these states, no dependences on the wavelengths of illumination were observed. This is consistent with the results of an optical study, where no evident charge transfer bands between the Ag ions and the DM species were observed in temperature-dependent polarized reflectance spectra [3].

The $\beta$–state occurred after illumination of Ag(DM)$_2$ in the pristine ($\alpha$–) state below 155°C. The $\beta$–state turned out to be produced through purely optical processes, i.e. photochemical reactions, and not accessible with any thermal treatment [4]. The $\beta$–state shared with the $\alpha$–state the appearances (SEM photographs), X-ray diffraction (XRD) pattern, elemental analyses (C, H, N(%)) and IR spectra (Fig. 2), though it exhibited different electrical behavior, Raman shifts and XPS. The N1s XPS peak in the $\beta$–state had a small shoulder corresponding to the charge transfer. The amount of charge transfer evaluated from XPS was consistent with that of Raman shift. While Ag(DM)$_2$ in the $\alpha$–state exhibited metallic electrical behavior down to $\sim$100 K, that in the $\beta$–state exhibited semiconducting behavior. Generally, the longer the illumination lasted, the higher the resistivity became. Judging from the Raman shifts, the formal charge of the DM species appeared to approach $\sim$0.40–0.35, where the illumination effects might saturate. After illumination ceased, the new semiconducting $\beta$–state lasted more than a half year, and it was never transformed into the $\alpha$–state again. There should be small but definite structural differences between the $\alpha$– and the $\beta$–states, which may make this transformation irreversible. Further detailed study is now in progress.
Other Related States

When the $\alpha$–state Ag(DM)$_2$ was heated at 155°C, it suddenly turned into a brown amorphous solid ($\gamma$–state). This state was a diamagnetic insulator. A series of detailed chemical, thermal, structural and spectroscopic analyses of the amorphous process proved that this transformation was a structural transition rather than a decomposition. Through the amorphization, not only the original well-defined shape of the single crystals of the $\alpha$–state, but also the mass of the sample, chemical stoichiometry and the molecular structure of the DM species were retained. The amorphization occurred sharply at 155°C irrespective of the atmosphere (under air or under dry nitrogen). The amorphous solid contained silver metal particles and DM molecules (X-ray absorption fine structures), but was insoluble to organic solvents. Phase separation did not occur to form bulk silver and neutral DM powder by any procedure. Comparison of IR and high resolution solid state NMR spectra clearly indicated that the neutral DM species had a different structure from the isolated neutral DM crystals.

When the $\alpha$–state Ag(DM)$_2$ was heated at ~ 160°C or strongly illuminated, it turned into a black solid ($\delta$–state) or white solid ($\varepsilon$–state). Both of them were nearly amorphous; the XRD powder patterns of them showed only broad and small peaks corresponding to the reflections of bulk silver. Although we could not find clear differences in production conditions of these two states yet. It was difficult to convert one of the two states to the other by any procedure. The $\delta$–state contained small particles of bulk silver with 9 nm in the average diameter, and was still rich in the DM species (IR and elemental analysis), which nearly corresponded to the original
stoichiometry (2:1). The ε–state was an aggregation of almost pure bulk silver particles (~65 nmφ) with a contamination of organic substances. The ε–state is considered to be produced by heating and decomposition of Ag(DM)$_2$. Diffuse scattering spectra (Fig. 3) suggested that the δ–state should be insulating, while the ε–state should be metallic.

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REFERENCES

Table 1 Different states derived from the pristine ($\alpha$-) Ag(DM)$_2$ by illumination or thermally treatments.

<table>
<thead>
<tr>
<th>states</th>
<th>colors</th>
<th>crystallinity</th>
<th>chemical formula</th>
<th>properties</th>
<th>typical conditions of sampling</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-</td>
<td>dark blue</td>
<td>crystalline</td>
<td>Ag(DM)$_2$</td>
<td>metallic</td>
<td>–</td>
</tr>
<tr>
<td>$\beta$-</td>
<td>dark blue</td>
<td>crystalline</td>
<td>Ag(DM)$_2$</td>
<td>semiconducting</td>
<td>368-700 nm 200 mW cm$^{-2}$, 30 min, $&lt; 155^\circ$C</td>
</tr>
<tr>
<td>$\gamma$-</td>
<td>brown</td>
<td>amorphous</td>
<td>Ag(DM)$_2$</td>
<td>insulating</td>
<td>155 $^\circ$C $\leq$</td>
</tr>
<tr>
<td>$\delta$-</td>
<td>black</td>
<td>amorphous$^1$</td>
<td>Ag(DM)$_n$ ; n $\leq 2$</td>
<td>$-^4$</td>
<td>155 $\leq T$ ($^\circ$C) $\leq \sim 200$</td>
</tr>
<tr>
<td>$\varepsilon$-</td>
<td>white</td>
<td>amorphous$^2$</td>
<td>Ag$^3$</td>
<td>$-^4$</td>
<td>$\sim 200$ $^\circ$C $\leq$</td>
</tr>
</tbody>
</table>

$^1$ with small crystallites of bulk Ag dispersed homogeneously  
$^2$ aggregation of small ($< 100$ nm) crystallites of bulk Ag  
$^3$ trace amount of C ($< 3\%$), H ($<0.3\%$) and N ($< 1\%$) were detected as a contamination.  
$^4$ conducting behavior is yet to be measured.
Figure Captions

Fig. 1  Molecular structure of DM.

Fig. 2  IR spectra in KBr pellets of (a) isolated neutral DM species, (b) $\alpha$-, (c) $\beta$-, (d) $\gamma$-, and (e) $\delta$–Ag(DM)$_2$, respectively.

Fig. 3  Diffuse scattering spectra of (a) isolated neutral DM species, (b) $\alpha$–, (c) $\gamma$–, (d) $\delta$–, and (e) $\epsilon$–Ag(DM)$_2$, respectively. The inset shows (d) and (e) spectra with $f(R)$ enlarged by 10 times.
Fig. 2 T. Naito et al.
( Fig. 3  T. Naito et al. )