JOURNAL OF MATERIALS SCIENCE **32** (1997) 6595–6600

Thermal and photo-induced surface damage in paratellurite

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Long-term operation of TeO_2 acousto-optical device is limited by the formation of surface damage caused by the He–Cd laser irradiation. Similar surface damage occurs during the heat treatment of the TeO_2 crystal at 350 °C. In this study, TeO_2 specimens after various surface treatments have been observed by electron microscopy and X-ray photoelectron spectroscopy. The variation of the transmittance for mechanically polished specimens has been measured *in situ* during heat treatments. It was found that the thermal surface damage at 350 °C was formed in the surface layer damaged by mechanical polishing. The mechanically damaged layer was amorphous and deficient in oxygen in the as-polished state. The electron microscopic observation revealed that the surface damage layer induced by heat treatments or by the ultraviolet light irradiation contained tellurium particles (20–40 nm) in diameter dispersed in the TeO_2 matrix. On annealing the TeO_2 specimen at 500 °C in air, however, the particles disappeared because of the melting, evaporation and oxidation of tellurium which restores the transmittance of the crystal. Based on the results, combined with the observation of surface damage induced by the visible light irradiation, a possible mechanism of the surface damage formation has been briefly discussed.

1. Introduction

Single-crystal paratellurite (α-TeO_2 tetragonal crystal, space group: $P4_12_12$) is a transparent insulator used for acousto-optical devices such as deflectors, light modulators and tunable optical filters [1, 2]. Recently, a practical problem has arisen in that long-term operation of TeO_2 acousto-optical device is limited by the formation of surface damage by the He–Cd laser irradiation. The surface damage has the following characteristics. (1) It is formed by a longer irradiation with the He–Cd laser (wavelength $\lambda = 441.6$ nm) than 10 h, with a power density higher than 10 W mm^{-2}, (2) there is no damage in the bulk crystal, and (3) the degree of damage is dependent on the surface preparation condition. For example, Fig. 1 shows an optical micrograph of the damaged region in (1 1 0) TeO_2 surface induced by He–Cd laser irradiation for 15 h [3]. Similar surface damage is caused by heat treatment at 350 °C. Because the surface damaged layer reduces the optical transmittance, it is called "surface optical damage (SOD)" here. However, the mechanisms of thermal or photo-induced SOD in TeO_2 have not yet been clarified.

In this work, we investigated the TeO_2 surfaces subjected to thermal or optical treatments by reflection electron diffraction (RED) observation, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The relation between the formation of thermal SOD and the surface preparation condition was studied by *in situ* measurements of the transmittance for the laser light. Based on the results obtained, the formation mechanism of SOD has been briefly discussed.

2. Experimental procedure

TeO_2 single crystals employed in this study were grown by the Czochralski technique from 99.9999% purity raw material. The growth axis was $\langle 1\,1\,0 \rangle$. Rectangular specimens measuring (3–8) × (3–10) mm^2 were cut from (1 1 0) oriented wafers with 1–2.5 mm thickness. Both front and back $\{1\,1\,0\}$ surfaces of the specimen were subjected to mechanical polishing or chemical etching until mirror surfaces were obtained. For mechanical polishing, 0.3 μm ZrO_2 particles were used on the wet polishing cloth. The polishing pressure was mainly 34 kPa. Chemical etching was carried out in 15% NaOH solution at room temperature.

To investigate thermal SOD in TeO_2, heat treatments at 350 and 500 °C were performed using a conventional furnace in the atmosphere of air or vacuum of 5×10^{-4} Pa. For the study of photo-induced SOD, mercury lamp (100 W) or halogen lamp (500 W) emission was irradiated on the specimens in air or in

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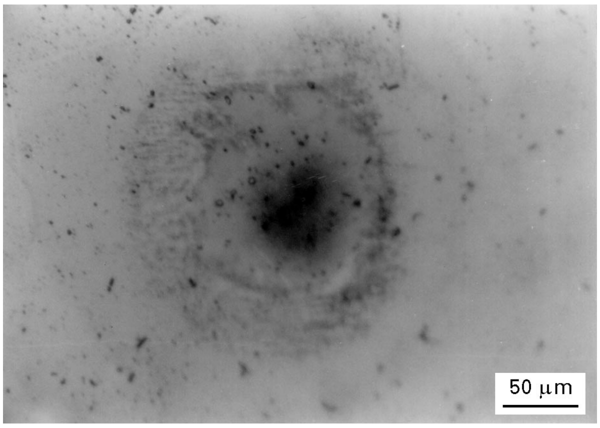

Figure 1 An optical micrograph of surface optical damage (SOD) induced by the He–Cd laser irradiation (45 mW) for 15 h.

vacuum for 50 h. The mercury lamp emission spectrum contains an ultraviolet component of wavelength shorter than 306 nm (the fundamental edge of TeO_2). On the other hand, the light emitted from halogen lamp ($\lambda > 500$ nm) is not absorbed by TeO_2. The surface of each specimen before and after heat treatment was observed by RED. For TEM observation, specimens containing SOD layers were thinned by the procedure reported elsewhere [4]. The transmission electron microscope (Hitachi, HU-12A) for RED and TEM observations was operated at 100 keV.

The transmittance of the specimen for 3 mW He–Ne laser light ($\lambda = 632.8$ nm) was monitored during the isothermal heat treatments in air. Two specimens polished under different pressures (34 and 14 kPa) were used to study the relation between the degradation of transmittance and the polishing pressure. The composition of the SOD layer was measured by XPS (ULVAC-PHI AES/ESCA, Model-255). For XPS analysis, an as-polished specimen, a specimen heat treated at 350 °C for 5 h in vacuum, and a specimen irradiated by mercury lamp in vacuum, were used. The excitation source for XPS was the MgK_α line (1252.9 eV).

3. Results

3.1. Optical microscopic observations

The optically flat and mirror surface of the TeO_2 acousto-optical device is generally obtained by mechanical polishing instead of chemical etching. This is because the latter method results in a less flat surface and often causes etch pitting. To clarify the effect of surface damage induced by mechanical polishing, specimens polished by both mechanical and chemical methods were subjected to the heat treatments for 5 h, or optical irradiation for 50 h. Each specimen was observed by an optical microscope to see the SOD formation. The specimen with SOD looked darker than the damage-free state to the naked eye. The qualitative results of the effects of various treatments on SOD formation can be summarized as follows.

1. Annealing at 500 °C in air or vacuum caused no SOD for either the chemically etched or mechanically polished specimens.
2. Heat treatments at 350 °C in air or vacuum caused no SOD in the chemically etched specimen, but caused SOD in the mechanically polished one. Therefore, it is concluded that SOD was formed in the specimen with surface mechanical damage. The specimen with SOD induced by the heat treatment in vacuum looked darker than that in air.
3. The specimen with SOD as stated in (2) regained its transparency on annealing at 500 °C in air.
4. Halogen lamp irradiation caused no SOD in any specimen. The temperature rise in the atmosphere was 70 °C.
5. Mercury lamp irradiation in air caused no SOD, either for the chemically etched or mechanically polished specimen. On the contrary, mercury lamp irradiation in vacuum caused SOD in both specimens. The temperature rise in the atmosphere was 110 °C.
6. SOD was easily removed by mechanical polishing of the surface layer of less than 1 μm.

3.2. Electron microscopic observations of SOD layers

Fig. 2 shows RED patterns of TeO_2 (1 1 0) surfaces, (a) in the as-polished state by mechanical method, (b) after heat treatment at 350 °C for 5 h in air, and (c) after heat treatments of (350 °C, 5 h + 500 °C, 5 h) in air. A halo pattern is seen in the specimen before the heat treatment (Fig. 2a). Therefore, the surface of the mechanically polished layer has damage in the amorphous state. The RED pattern in (b) shows that the polycrystalline diffraction rings from TeO_2 and tellurium co-existed, which indicates that the SOD layer obtained by 350 °C heat treatment, contains tellurium precipitates. Patterns similar to Fig. 2b were observed both in the specimen heat treated at 350 °C in a vacuum for 5 h, and in that irradiated by a mercury lamp in vacuum. On the other hand, TeO_2 single crystalline pattern is seen in Fig. 2c. This agrees with result (3) in Section 3.1, showing the recovery of SOD by 500 °C annealing in air.

Transmission electron micrographs of the mechanically polished specimen followed by heat treatment at 350 °C in vacuum are shown in Fig. 3. Fig. 3a shows a bright-field image of the SOD layer and (b) is a corresponding dark-field image taken by the Te (1 0 0) reflection. Because bright spots in (b) coincide with some black dots in (a), the black dots in (a) are identified as tellurium precipitates with 20–40 nm diameter. In the specimen irradiated by a mercury lamp in vacuum, tellurium precipitates with a similar size were observed in higher density. These results clearly show that SOD induced by the heat treatment at 350 °C or mercury lamp irradiation is composed of tellurium precipitates and a TeO_2 matrix.

It is known that tellurium crystal has a melting point of 449.8 °C and a high vapour pressure (1 atm at 994 °C) [5]. Tellurium is immiscible with TeO_2 and easily oxidized in air to form TeO_2 [5]. Therefore, it is possible for tellurium precipitates to disappear from the SOD layer at 500 °C by evaporation or oxidation.

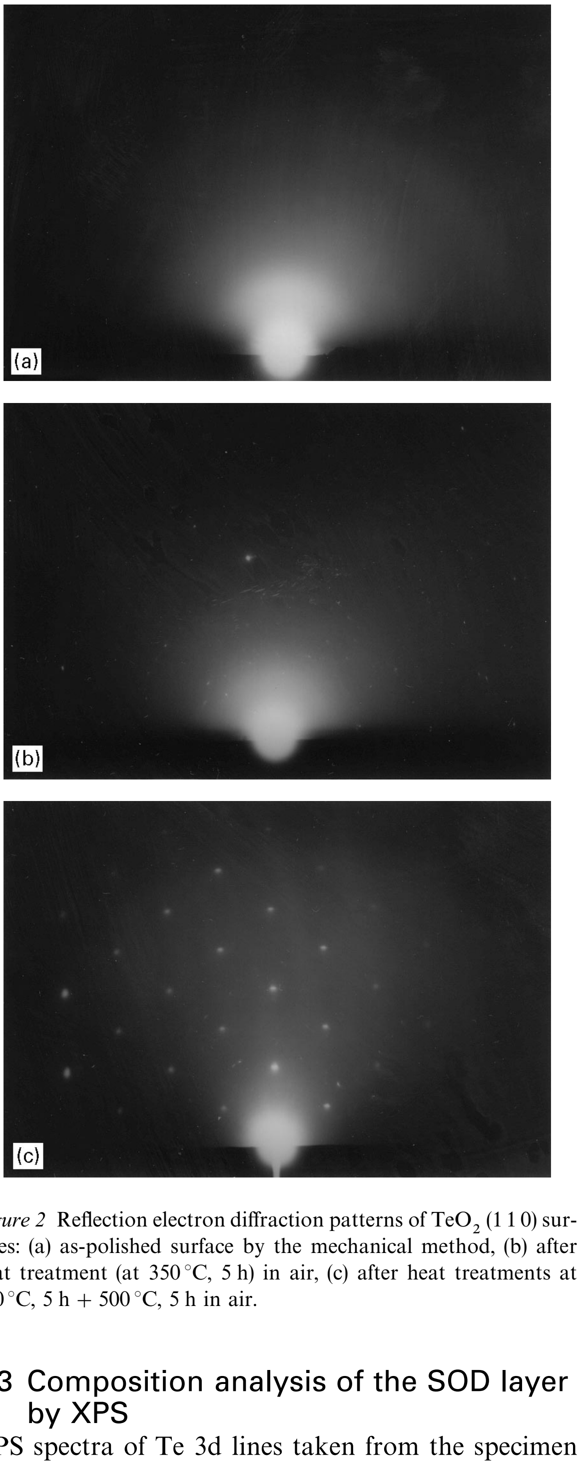

Figure 2 Reflection electron diffraction patterns of TeO_2 (1 1 0) surfaces: (a) as-polished surface by the mechanical method, (b) after heat treatment (at 350 °C, 5 h) in air, (c) after heat treatments at 350 °C, 5 h + 500 °C, 5 h in air.

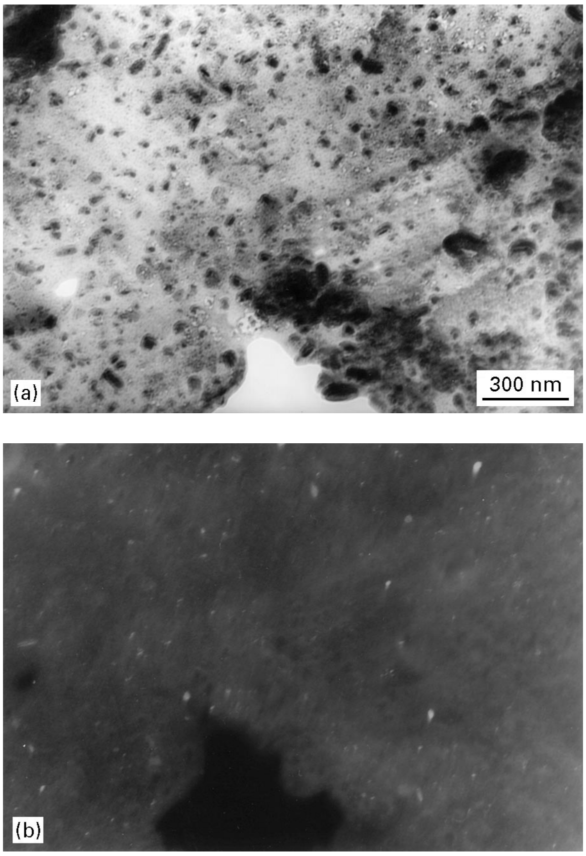

Figure 3 Transmission electron micrographs of the SOD layer in TeO_2 after heat treatment at 350 °C, 5 h in vacuum: (a) bright-field image, (b) dark-field image obtained by Te (1 0 0) reflection.

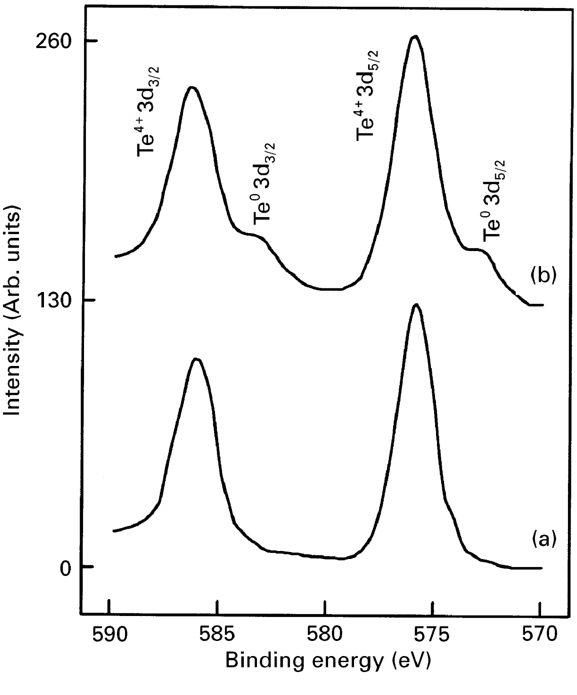

Figure 4 XPS spectra of the SOD layer in TeO_2 after heat treatment at 350 °C, 5 h in vacuum: (a) at the surface, (b) about 96 nm below the surface after Ar^+ sputtering for 3 min.

3.3 Composition analysis of the SOD layer by XPS

XPS spectra of Te 3d lines taken from the specimen heat treated at 350 °C in vacuum are shown in Fig. 4. (a) and (b) were taken at the specimen surface and after 3 min Ar^+ sputtering (96 nm below the surface), respectively. Two sets of XPS peaks are seen in Fig. 4b. Te^0 lines ($Te^0 3d_{3/2}, Te^0 3d_{5/2}$) are due to elemental tellurium atoms and Te^{4+} lines ($Te^{4+}3d_{3/2}, Te^{4+}3d_{5/2}$) to tellurium atoms bonded with oxygen in TeO_2. These spectra show that the SOD layer consists of the mixture of tellurium and TeO_2, which is consistent with the TEM results. The smaller Te^0 peaks at the surface (Fig. 4a) than those in (b) are attributable to the effect of natural oxidation in air. The composition x in SOD layer (TeO_x) can be calculated from the area ratio under the Te^0 and Te^{4+} peaks after decomposing the peaks [6]. Fig. 5 shows the depth profiles of x in three kinds of TeO_2 specimens. The oxidized layer is seen at the surface region ($\sim$100 nm) in each specimen. In the specimen heat treated at 350 °C in vacuum (Fig. 5b), the elemental tellurium is distributed homogeneously in the SOD layer. However, the tellurium concentration in the specimen irradiated by the mercury lamp (Fig. 5c) decreases with depth beneath

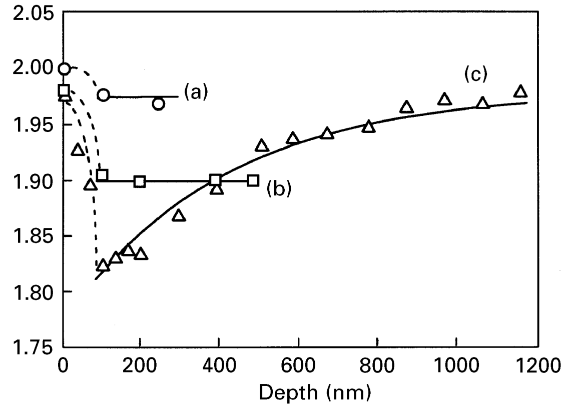

Figure 5 Depth profiles of the composition x in the TeO_x surface region: (a) as-polished surface by the mechanical method, (b) after heat treatment at 350 °C, 5 h in vacuum, (c) after mercury lamp irradiation for 50 h in vacuum.

the oxidized layer. The elemental tellurium is also seen in the as-polished specimen, showing the mechanically damaged layer is deficient in oxygen ($x \sim 1.975$).

3.4. *In situ* measurements of the transmittance during heat treatments

The transmittance for the He–Ne laser light is measured during the isothermal heat treatment at 350 °C in air. Fig. 6 shows the variation in the transmittance of the mechanically polished specimens. The polishing pressure is 14 kPa in (a) and 34 kPa in (b). The decrease in transmittance is larger for the specimen polished with the larger pressure and saturated after about 2 h. Because TeO_2 crystal is transparent for visible light, the thicker SOD layer results in the larger decrease of transmittance. It is considered that the depth of the mechanically damaged layer corresponds to the thickness of the SOD layer.

Fig. 7 shows the restoration of the transmittance by annealing at 450, 500 and 550 °C. In this experiment, the mechanically polished specimens after heat treatment at 350 °C for 5 h in vacuum were used as the initial state. The transmittance in the initial state is taken as 1. It is seen that the transmittance is restored faster at the higher annealing temperature. The restoration curve at 450 °C shows a dip at the first stage of restoration. From the optical microscopic observation, the surface roughening by the evaporation of tellurium precipitates is deduced to be the cause. No dip is observed in the restoration curve for the specimens annealed at 500 and 550 °C. Probably, the tellurium precipitates evaporated before the temperatures of 500 or 550 °C were reached. The increase in transmittance after the tellurium evaporation may be due to the oxidation of the residual tellurium particles or thermal polishing of the surface roughness.

4. Discussion

4.1. Optical properties of the SOD layer

The specimen with SOD showed degradation of the transmittance for visible light. Because TeO_2 bulk is transparent for visible light, the transmittance is reduced only in the SOD layer, that is the mixture of tellurium precipitates and TeO_2 matrix. The cause of the decrease in transmittance is due either to the absorption or to the scattering of the light by tellurium particles. In this section, we estimate the contribution of absorption and scattering for the trasmittance degradation of the specimen with SOD induced by the heat treatment at 350 °C for 5 h in vacuum.

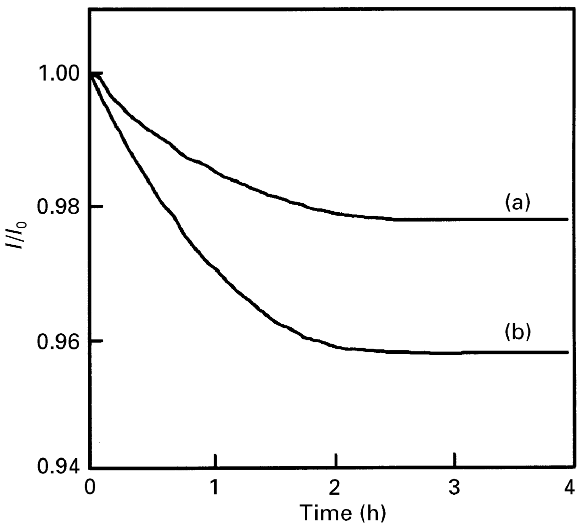

Figure 6 Reduction of the transmittance of TeO_2 during the isothermal heat treatment at 350 °C in air. TeO_2 specimens were mechanically polished under a pressure of (a) 14 kPa and (b) 34 kPa. The incident light was He–Ne laser.

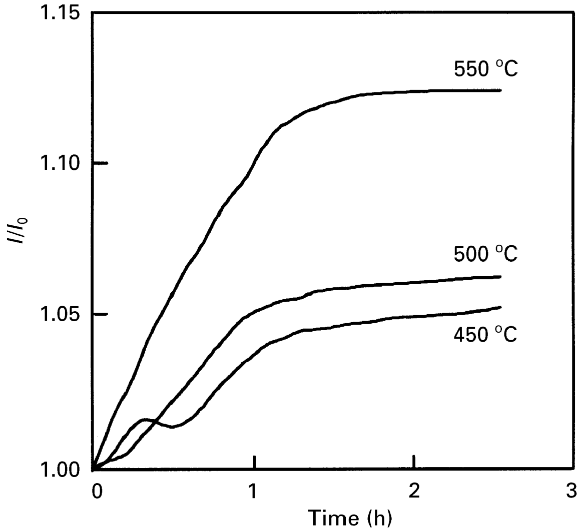

Figure 7 Restoration of the transmittance of damaged TeO_2 during isothermal annealing in air. The initial transmittance for each TeO_2 specimen with an SOD layer is taken as 1. SOD layers were induced by the heat treatment at 350 °C for 5 h in vacuum for the mechanically polished specimens. The incident light was He–Ne laser.

Because the wavelength of the He–Ne laser (632.8 nm) is much larger than the diameter of the tellurium particles, the light scattering by tellurium particles is described in terms of Rayleigh scattering [7]. The scattering coefficient, S is given by

$$S = \frac{128\,\pi^4 r^3 q n^4}{3\lambda_0^4}\left(\frac{M^2-1}{M^2+2}\right)^2 \qquad (1)$$

where r is the radius of tellurium particles, q the volume fraction of tellurium particles, n the refractive index of the TeO_2 matrix, λ_0 the wavelength of the incident light, M the ratio of the refractive indices of TeO_2 and Te. The TEM observation in Fig. 3 and the analysis of the XPS data in Fig. 4 revealed that $r = 10\text{–}20$ nm and $q = 0.037$, respectively. Using the complex refractive indices of TeO_2 ($n = 2.26 - 0i$) and tellurium ($n_{Te} = 5.9885 - 2.4129i$), S was obtained to be 400 cm^{-1}.

Substituting the mixed layer of tellurium and TeO_2 to an optically equivalent homogeneous layer and using the Lorentz–Lorenz relation [7], the complex refractive index of the SOD layer ($N_c = n_c - ik_c$) is given by the following equation.

$$\frac{N_c^2 - 1}{N_c^2 + 2} = q\frac{n_{Te}^2 - 1}{n_{Te}^2 + 2} + (1 - q)\frac{n^2 - 1}{n^2 + 2} \qquad (2)$$

For the specimen damaged by the heat treatment at 350 °C for 5 h in vacuum, $n_c = 2.312$ and $k_c = 0.0067$ are obtained from Equation 2. The absorption coefficient of the SOD layer is then given by the relation

$$\alpha = 4\pi n_c k_c / \lambda_0 \qquad (3)$$

to be $\alpha \sim 3000$ cm^{-1}. Because the absorption coefficient is about seven times larger than the scattering coefficient, the decrease of the transmittance is attributed to the absorption by the tellurium precipitates.

4.2. The structure of the SOD layer

The volume fraction of tellurium precipitates in the thermally-induced SOD layer is uniform in the depth direction (Fig. 5b; $x = 1.9$). Hence, the relation between the thickness of the SOD layer, d, and the optical transmittance, T, is described as

$$T = \frac{I}{I_0} = \exp[-(\alpha + S)d] \qquad (4)$$

here, I is the intensity of the transmitted light and I_0 the incident light intensity. On the specimen heat treated at 350 °C for 5 h in vacuum, the transmittance for the He–Ne laser light was about $T = 0.78$. Using this value and the results in Section 4.1, d was calculated to be 740 nm from Equation 4.

Considering that SOD layers exist in both front and back surfaces and have the oxidized region ($\sim$ 100 nm from Fig. 5b), the thickness of the mechanically damaged layer is estimated to be about 470 nm when the polishing pressure is 34 kPa. At the lower polishing pressure of 14 kPa, the thickness of the mechanical damage is about 290 nm. The estimated depth of the mechanical damage is of the same order as the average diameter of the polishing particles ($\sim$ 300 nm). This agrees with the reported results on the damaged layer thickness in the brittle crystals like silicon [8].

Based on these, the structure of the SOD layer induced by the heat treatment at 350 °C or by the mercury lamp irradiation is schematically illustrated in Fig. 8. The thermal SOD at 350 °C has a layer with uniform distribution of tellurium precipitates (20–40 nm diameter) beneath the 100 nm thick oxidized layer. The thickness of the precipitated layer is about 370 and 190 nm for the polishing pressures of 34 and 14 kPa, respectively. SOD by mercury lamp irradiation also has 100 nm thick oxidized layer and has the tellurium precipitated layer with decreasing density along the depth direction. Presumably, this profile corresponds to the distribution of the absorbed ultraviolet light intensity in TeO_2. The volume fraction of the tellurium precipitates in Fig. 8 was estimated from the depth profile of the composition by XPS analysis (Fig. 5).

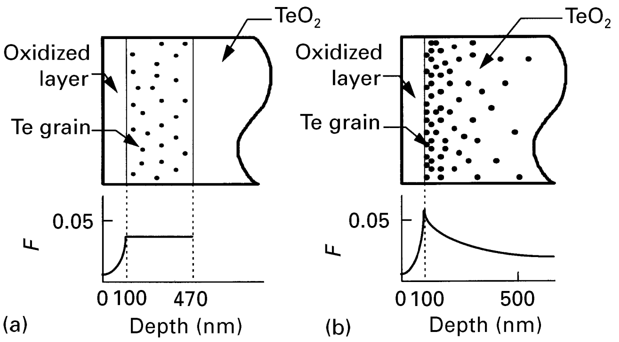

Figure 8 Schematic illustrations of the SOD layer and volume fraction of tellurium, F, in TeO_x (a) SOD induced by the heat treatment at 350 °C in the mechanically polished specimen (polishing pressure 34 kPa), (b) SOD induced by mercury lamp irradiation for 50 h in vacuum.

4.3. Mechanism of SOD formation by visible light irradiation

The spectrum of the mercury lamp contains ultraviolet light (with larger energy than the band gap of TeO_2:4.05 eV) which is absorbed by TeO_2 and is considered to break the Te–O bond. It is therefore possible that mercury lamp irradiation causes the oxygen deficiency and tellurium precipitation in the surface layer of TeO_2, independently of the presence of the mechanical damage. However, the specimen irradiated by the mercury lamp in air showed no SOD. This is probably due to the immediate oxidation of tellurium by the ultraviolet irradiation. It has been reported that oxygen activated by ultraviolet light caused the rapid oxidation of tellurium thin films [9].

On the contrary, visible light is not absorbed by TeO_2. Therefore, it is considered that SOD induced by the visible light is related to the presence of mechanical damage. First we estimated the temperature rise by the visible light irradiation based on the solution for the equation of heat conduction given by Young and Tillar [10]. He–Cd laser ($\lambda = 441.6$ nm) irradiation with 45 mW power and 55 μm beam size was considered. Even if 100% of the laser light was absorbed by tellurium in the mechanically damaged layer, the temperature rise was 22 °C. Hence, the formation of SOD by visible light is not due to the thermal effect.

Because the layer mechanically damaged by polishing is in the amorphous state, the high density of unstable Te–O bonds is expected to exist in the layer. Possibly, the photon energy of the He–Cd laser (2.8 eV) is enough to break weak Te–O bonds in a-TeO_x and cause oxygen deficiency. The activation energy of the tellurium precipitation in the SOD layer was estimated to be 1.07 eV by analysing the reduction curves of transmittance at 325, 350 and 375 °C (only one of them was shown in Fig. 6). Hence, the activation energy of tellurium diffusion in TeO_2 should be equal to or less than 1.07 eV. The absorbed photon energy (2.8 eV) of the He–Cd laser can be used for the activation of tellurium diffusion. This makes it possible for precipitation of tellurium particles to occur under visible light irradiation. These mechanisms may explain the formation of SOD under the prolonged irradiation of a He–Cd laser in the mechanically damaged layer of TeO_2.

5. Conclusions

To clarify the mechanism of SOD formation in TeO_2 single crystals, electron microscopic observation and XPS analysis of the SOD layer were carried out. The variation in the optical transmittance was also measured *in situ* during the heat treatment. From the observations on the specimens with various surface treatments, the following conclusions were drawn.

1. SOD by heat treatment at 350 °C or visible light irradiation, is formed in the damaged layer by mechanical polishing.
2. The mechanically damaged layer is in the amorphous state and is described as a-TeO_x ($x < 2$).
3. The SOD layer contains tellurium precipitates (20–40 nm diameter) dispersed in the TeO_2 matrix. Tellurium particles absorb visible light. The thickness of the SOD may correspond to that of the mechanical damage.
4. Probably, weak Te–O bonds in the mechanically damaged layer are broken by the 350 °C heat treatment or by the visible light irradiation, which cause the oxygen deficiency in the surface layer. The SOD layer is formed by the precipitation of tellurium particles.
5. The SOD layer disappears on annealing at 500 °C in air. Tellurium particles melt, evaporate and are oxidized by annealing at 500 °C in air.

From these results, the heat treatment at 500 °C in air after mechanical polishing is found to be useful in avoiding SOD formation. Finally, this procedure has been effectively used to avoid SOD formation in TeO_2 acousto-optical devices under normal operating conditions.

Acknowledgements

The authors thank Mr F. Tanaka, Matsushita Electronics Components Co., Ltd and Mr K. Kanayama of Mitsui Petrochemical Industries, Ltd, for their valuable discussions and supplying TeO_2 single crystals. They also thank Professor K. Koterazawa and Dr S. Inoue for their kind cooperation in the XPS measurements.

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Received 3 January 1996
and accepted 4 April 1997