4) PbO , Nb_2O_5 , TiO_2 等を含有する高屈折高分散ガラスにおいて, n_D が 1.95 より大きい場合, ν_D が 22 より小さい場合, または λ_0 が 170 nm より長波長にある場合には, ガラスの吸収端 $\lambda_{\text{abs}=1}$ は 370 nm より大きく, このようなガラスでは無色のガラスを得ることがほとんど不可能に近い。

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論 文・Paper

Formation Process and Optical Absorption Edge of Amorphous As_2S_3 Films

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For amorphous As_2S_3 films deposited at temperatures from -170°C to 170°C , optical absorption edges, IR spectra, and thermally induced changes of these optical properties were studied as a function of the deposition temperature. As-deposited films contained As_4S_4 and sulfur components, the amount of which was highly dependent on the deposition temperature; as the deposition temperature decreased, the amount of these components increased. From these observations, the decomposition of As_2S_3 glass to As_4S_4 and sulfur components in the evaporation process was proposed. Annealing of as-deposited films at temperatures near glass transition caused the reaction of residual As_4S_4 and sulfur components, accompanying the shift of absorption edge to lower photon energies. From the compositional analysis, it was found that the films deposited at temperatures higher than 100°C was sulfur-poor compared with the stoichiometric composition. The dependence of optical band gap on the deposition temperature for annealed films was explained in terms of the remaining As_4S_4 component and/or sulfur deficiency in the films.

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As_2S_3 非晶質薄膜の生成過程と光学吸収端

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As_2S_3 非晶質薄膜の光学吸収端, IR スペクトル, 及びこれら光学的性質の熱処理による変化と, 薄膜の析出温度との関係を, $-170^\circ\sim 170^\circ\text{C}$ の温度範囲で調べた。蒸着したままの薄膜中には, As_4S_4 と硫黄成分が残存しており, それらの量は析出温度が低くなるに従って増加した。このことから, As_2S_3 ガラスは蒸着の際には As_4S_4 と硫黄成分に分解すると推察した。薄膜をガラス転移温度付近の温度で熱処理すると, 残存していた As_4S_4 と硫黄成分が反応し, As_2S_3 バルクガラスに非常によく似た構造に変化した。これが, 熱処理による光学吸収端の低光子エネルギー方向への移動の原因であると考えられる。得られた薄膜の組成分析の結果, 析出温度が 100°C 以上の薄膜では, 硫黄成分が化学量論組成よりも不足していることが見いだされた。したがって, 熱処理薄膜に

おける光学的バンドギャップの析出温度依存性は、 As_4S_4 成分の残存とイオウ成分の不足、あるいはそのいずれかに起因しているものと考えられる。

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Key-words : Amorphous chalcogenide films, Chalcogenide glasses, IR spectra, Absorption edge shift

1. Introduction

Amorphous chalcogenides of group 4 B and 5 B elements have been attracting much attention in this decade as an image-storage medium, as well as semiconductors, ever since the efficient storage of a hologram on amorphous As_2S_3 films was reported¹⁾. Several of chemical and physical properties of these materials vary with light illumination and annealing^{2)~6)}. These phenomena are applicable to image storage, photoresist, and so on.

The optical absorption edge of chalcogenide films is one of properties exhibiting remarkable changes by annealing and light illumination^{4), 7)}. Annealing of as-deposited films shifts the absorption edge irreversibly to lower photon energies and subsequent light illumination causes further shift of the edge to the same direction. The latter change is referred to as "photo-darkening" and reversibly recovered by annealing. The mechanism of these thermally and optically induced changes, however, has not been completely explained.

In a previous note on IR spectra of amorphous As_2S_3 films deposited at different temperatures, we reported that the structure of as-deposited films was highly dependent on the deposition temperature⁸⁾. There are some papers on thermally induced change in structure of evaporated As_2S_3 films⁹⁾. However, the relation between optical properties and structures has not been systematically studied. The present paper describes optical absorption edge of these films and its thermally induced change as a function of the deposition temperature. Based on the structural information from the IR spectra, a formation process of amorphous As_2S_3 films and a mechanism of thermally induced change in the absorption edge are discussed.

2. Experimental

The films were evaporated at a rate of 1.5 ~ 2 $\mu\text{m}/\text{min}$ in a vacuum of $\sim 2 \times 10^{-6}$ Torr on cover-glasses or silicon wafers for the measurements of optical transmission or IR spectra,

respectively. Precautions were taken to heat the quartz-glass crucible containing pulverized As_2S_3 glasses at nearly the constant temperature (400°~500°C) for each run. The deposition temperature of the films was varied in the range of -170°C to 170°C by controlling the substrate temperature to an accuracy of $\pm 5^\circ\text{C}$.

The optical transmission of the films was measured at room temperature using the system reported previously¹⁰⁾; transmission of even $\sim 10^{-4}\%$ could be detected. Optical absorption coefficients were evaluated from the transmission data, taking account of film thickness and reflectance at the surfaces. IR spectra were measured using an IR spectrophotometer (JASCO, DC-700 G). Annealing was carried out in a dry nitrogen stream at 200°C for 1 h. The composition of the films obtained was analyzed using an X-ray micro-analyzer (JEOL, JSM-50 A).

3. Results

3.1 Optical absorption edge of evaporated As_2S_3 films

3.1.1 Thermally and optically induced changes in absorption edge

Figure 1 is an example of the dependence of absorption coefficient α on photon energy $h\nu$ in the vicinity of optical absorption edge for the film at various stages: as-deposited at 5°C (a), annealed at 200°C for 1 h (b), and illuminated at -160°C (c). Annealing at 200°C, which is close to the glass transition temperature reported for As_2S_3 bulk glass^{11), 12)}, shifts irreversibly the absorption edge to lower energies ((a)→(b)) and subsequent illumination at -160°C of light from xenon lamp (300 W) causes further shift of the edge to lower energies ((b)→(c)). The latter change caused by illumination can be recovered by annealing at 200°C ((c)→(b)). The present paper is mainly concerned with the irreversible change by heat-treatment ((a)→(b)). Here the photon energy extrapolated to zero of $\sqrt{\alpha h\nu}$ vs. $h\nu$ plots is adopted as the optical band

gap E_g^{opt} , as shown in the figure by a dashed line.

3.1.2 Dependence of optical band gap on deposition temperature

The optical band gap E_g^{opt} is plotted against the deposition temperature T_d in Fig. 2 for as-deposited (open circles) and annealed films (closed circles). The optical band gap of films deposited at temperatures lower than 5°C is almost constant (~ 2.33 eV). With further

Fig. 1. Optical absorption coefficient vs. photon energy in the vicinity of absorption edge and its changes by annealing and light illumination for the amorphous As_2S_3 film deposited at 5°C.

Fig. 2. Optical band gap of as-deposited (open circles) and annealed films (closed circles) as a function of deposition temperature.

increase in T_d , E_g^{opt} increases, passes a maximum (~ 2.38 eV) at around $T_d = 120^\circ\text{C}$, and then decreases. On the other hand, annealing at temperatures near glass transition reduces E_g^{opt} for all the films. The optical band gap of annealed films remains constant (~ 2.32 eV) for $T_d < 80^\circ\text{C}$ and then monotonously increases with increase in T_d . It is noticeable that E_g^{opt} of the film deposited at 170°C is little reduced by annealing.

3.2 IR spectra of evaporated As_2S_3 films

3.2.1 IR spectra of as-deposited films

Figure 3 shows IR spectra in the range of 450 cm^{-1} to 200 cm^{-1} for the films as-deposited at different T_d . There are two strong absorptions at 375 cm^{-1} and 340 cm^{-1} and a shoulder at 310 cm^{-1} for the film deposited at -170°C . With increase in T_d , the latter shoulder grows to a strong absorption which is observable in As_2S_3 bulk glass¹³⁾. As previously reported⁸⁾, the two absorptions at 375 cm^{-1} and 340 cm^{-1} agree in wavenumber with the absorptions characteristic of crystalline $\beta\text{-As}_4\text{S}_4$: 375 cm^{-1} and 345 cm^{-1} ¹⁴⁾. On the other hand, the absorption at 310 cm^{-1} is assigned to the anti-symmetric As-S stretching mode of AsS_3 pyramidal structural units in As_2S_3 bulk glass¹³⁾. The results therefore suggest the presence of

Fig. 3. IR spectra of As_2S_3 films as-deposited at different temperatures.

Fig. 4. IR spectra of As_2S_3 films deposited at temperatures shown in the figure and subsequently annealed at 200°C for 1 h. The spectrum represented by a broken line is shown for comparison with the as-deposited film; the spectrum is cited from Fig. 3 ($T_d=5^\circ\text{C}$) as an example.

As_4S_4 component in as-deposited films, the amount of which decreases with increase in T_d .

3.2.2 IR spectra of annealed films

IR spectra of annealed As_2S_3 films with different T_d are shown in **Fig. 4**. Comparison of the spectra with those in **Fig. 3** indicates that annealing intensifies the absorptions at 310 cm^{-1} , whereas it weakens the absorptions at 375 cm^{-1} and 340 cm^{-1} . Especially, for the films with rather low T_d ($<100^\circ\text{C}$), the absorptions originated from As_4S_4 component have disappeared and the absorption at 310 cm^{-1} dominates; the resultant spectra are very similar to that of As_2S_3 bulk glass. However, it should be noticed that for the films with higher T_d than 100°C , the change in IR spectra is slight and the absorption at 375 cm^{-1} is still appreciable.

4. Discussion

4.1 Formation process of amorphous As_2S_3 films

Evaporated films are formed via several steps; (1) evaporation of gaseous species, (2) deposition of the gaseous species on a substrate, and (3) reaction of the deposited species on the substrate to form a film. The substrate

temperature or deposition temperature is a principal factor to govern the processes (2) and (3). In particular, when the substrate is kept at low temperatures, the reaction of deposited species (process (3)) is suppressed, and hence it is expected that deposited species remain in the films.

The result in **Fig. 3** shows that as-deposited films contain an increasing amount of As_4S_4 component with decrease in T_d . This observation reveals the following decomposition occurs in the evaporation of As_2S_3 glass,

Sulfur component in as-deposited films was not confirmed directly from IR spectra. Its presence, however, is reasonably supposed from the facts that IR spectra of the films deposited at low temperatures changed to those of stoichiometric As_2S_3 glass after annealing and that the atomic ratio of As to S in the films was nearly 2/3 except for the films deposited at rather high temperatures, as described in 4.2. Deposited As_4S_4 and sulfur components on a substrate react to form As_2S_3 amorphous films, the degree of the reaction being of great dependence on the deposition temperature: decrease in the deposition temperature depresses the reaction of As_4S_4 with sulfur components.

4.2 Annealing effect on the structure of As_2S_3 films

Annealing of the evaporated films weakens the IR absorptions at 375 cm^{-1} and 340 cm^{-1} due to the As_4S_4 component. This indicates that annealing facilitates the reaction of residual As_4S_4 and sulfur components and thereby causes a structural transformation in the films to the structure very similar to that of As_2S_3 bulk glass. As already pointed out, for the films deposited at temperatures higher than 100°C , the absorptions originated from the As_4S_4 component are appreciable even after the sufficient annealing. This observation is associated with deviation in composition of these films from stoichiometry. In **Fig. 5**, the $\text{As K}_\alpha/\text{S K}_\alpha$ ratio for the four films with different T_d is plotted on the calibration line which was determined for As_4S_4 crystal and bulk glasses As_2S_3 and As_3S_7 . Sulfur is obviously poor for the films deposited at higher T_d than 100°C . It is therefore concluded that the As_4S_4 component remains unreacted in annealed films with high T_d due to sulfur deficiency from

Fig. 5. Plot of the As K_{α} /S K_{α} ratio against the weight ratio of As to S. The calibration line was determined for As_4S_4 crystal and bulk glasses As_2S_3 and As_3S_7 .

stoichiometry.

4.3 Optical band gap of as-deposited films and its thermally induced change

As discussed above, as-deposited As_2S_3 films contain residual As_4S_4 and sulfur components. Accordingly, the measured E_g^{opt} of as-deposited films is the apparent optical band gap related to these components. Details of the contribution of these components to the optical band gap are not clear at present stage, but would be complex because the dependence of E_g^{opt} on T_d is not monotonous. The decrease in E_g^{opt} for as-deposited films with higher T_d than 120°C can be explained by considering that these films were exposed to annealing to some extent during deposition.

The dependence of E_g^{opt} on T_d for annealed films can be understood in terms of the variation in composition of the films; the increase in E_g^{opt} for the films with higher T_d than 100°C is possibly ascribed to the remaining As_4S_4 component and/or sulfur deficiency, as revealed in IR spectra and compositional analysis.

5. Conclusions

For amorphous As_2S_3 films deposited on temperature-controlled substrates, optical absorption edges, IR spectra, and thermally induced changes of these optical properties

were studied as a function of the deposition temperature. The formation process of the films was discussed on the basis of the experimental results. The following conclusions were obtained:

(1) As-deposited films contain As_4S_4 and sulfur components, the amount of which is highly dependent on the deposition temperature; as the deposition temperature decreases, the amount of these components increases. From these observations, the decomposition of As_2S_3 glass to As_4S_4 and sulfur components in the evaporation process was proposed.

(2) Annealing at temperatures near glass transition causes the reaction of residual As_4S_4 and sulfur components in as-deposited films, accompanying the shift of absorption edge to lower photon energies.

(3) Compositional analysis proved that the films deposited at temperatures higher than 100°C was sulfur-poor compared with the stoichiometric composition. The dependence of optical band gap on the deposition temperature for annealed films was explained in terms of the remaining As_4S_4 component and/or sulfur deficiency in the films.

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実験・技術・調査報告・Report

セラミックスのダイヤモンド砥石による切断加工

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セラミック材料の加工法を確立するため、その一部であるダイヤモンド砥石による切断加工法において、ホットプレス窒化ケイ素の切断加工条件の選定とその問題点について検討した。切断加工にはメタルボンドとレジノイドボンドの両ダイヤモンド切断砥石を用い、加工中の負荷電流の測定と同時にこれに伴う砥石表面の砥粒の摩耗の進行を走査型電子顕微鏡で観察した。

この結果、次の結論を得た。

- 1) ホットプレス窒化ケイ素の切断加工においては砥石外周面及び側面上のダイヤモンド砥粒の摩耗が進行し、加工能率を著しく低下させるため目直し作業が不可欠である。
- 2) 砥石側面上の砥粒の摩耗によって負荷電流は大幅に増加するが、この砥石側面に 1/100 程度のテーパを付けることにより摩耗を防ぎ目直し間切断面積を大幅に上げることができる。
- 3) 切断加工エネルギーは、砥石切り込み深さが小さいほど少ない。(1981 年 4 月 22 日受付)

Cutting Process of Ceramics with Diamond Wheel

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In order to establish the mechanical processing technique of ceramics, the cutting conditions and the other problems in the abrasive machining of hot-pressed silicon nitride with the cutting wheel are discussed. As the cutting tool, metal and resinoid bonded diamond wheels were used, and the load current was measured and the worn grains on the surface of the wheel were observed with SEM. The main results obtained are as follows:

- 1) The diamond grains on the external and the side surfaces of a wheel wore out remarkably in the cutting process of hot-pressed Si_3N_4 . Then the cutting load current increased on a large scale as the wear of grains. Therefore, the cutting efficiency lowered, and the dressing was indispensable in the cutting process with a diamond wheel.
- 2) The wear, however, was prevented by giving the taper of the order of 1/100 on the side surface, and the redress life of the cutting wheel increased with this taper of both sides.
- 3) The cutting energy per unit area decreased as decreasing of depth of cut.

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Key-words : Cutting process, Silicon nitride, Diamond wheel, Tapered cutting wheel, Grinding force

1. 緒 言

工業材料としてのセラミックスは、一般的に、耐熱性、耐食性、耐摩耗性等の点ですぐれた性能を示し、特

に最近の窒化ケイ素ではその強度の向上も著しく^{1),2)}、これらの特長を生かした構造材料への利用に対する期待が大きい。一方、これらの材料の新たな分野での利用を