Effect of Thermal Annealing on the Characteristics of Bi-Sb Thin Film Structure

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Abstract—**In this study, Bi-Sb thin film structure was prepared by thermal evaporation method. The electrical, optical transmission and structural characteristics of the prepared samples were introduced before and after thermal annealing process. At temperature of 500 °C, the absorption of the structure was improved to reach 97% at near-infrared region. As well, the thermal annealing caused to reduce the bulk resistance of the Bi-Sb thin film structure. The mor-phology of Bi-Sb structure was also improved by thermal annealing as characteristic islands of the structure appear clearly in form hexagonal areas distinct from each other. This study is aiming to examine such structures if they are employed as photonic devices such as photodetectors, LED's and optical switches.**

Index Terms—**Bi-Sb structure, thin films, vacuum evaporation, thermal annealing**

I. INTRODUCTION

The study of Bi, Sb and their alloys is interesting because of their semi-metallic behavior, and the low Fermi energy and small effective mass of their conduction electrons. Bi and Sb are both group V elements, which have the same trigonal crystal structure and are completely soluble in each other in the solid state [1-3].

The addition of Sb to Bi does not alter either the crystal structure or the quality of positive or negative charge carrier concentrations. The change in the properties of Bi-Sb alloys and a transition from metallic to semi-conducting behavior arise because of the modification of the band structure (separation of bands) due to Sb addition. This is not the case for other Bi alloys like Bi-Pb and Bi-Sn, where the added element belongs to a group other than group V, not only the band structure but also the equality of positive and negative charge carrier concentration changes. The study of Bi-Sb alloys in the thin film state is especially interesting as the small effective mass of the conduction electrons and low Fermi energy mean that quantum size effects appear at small film thicknesses [4,5].

In the thin film state, bismuth behaves like a narrow band gap semiconductor under suitable conditions. Also, as in general vacuum-deposited bismuth films are either polycrystalline or have a fibrous orientation, there will be a large number of grains in the film and hence the electron mean free path may be limited by the size of the grains. As a consequence, Bi films may exhibit anomalous behaviour with temperature, which will be strongly influenced by the vacuum deposition conditions [6,7].

The electrical resistivity and thermo-electric power studies made recently on antimony and bismuth films have shown large inconsistencies. This could be due to different evaporating conditions and annealing followed. Recent measurements of the electrical resistivity of thin Sb and Bi films deposited at a pressure of 10^{-10} torr are worth mentioning. It was found the crystal size could be kept constant with increasing thickness by using appropriate heat treatments and an epitaxial technology [8-10].

II. EXPERIMENT

Thin films of high purity (99.999%) antimony were deposited on glass slides using thermal evaporation system under vacuum of 10^{-6} torr. Thickness of the deposited

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film was 150 nm. After performing the necessary measurements on the antimony films, thin film of high purity (99.99%) bismuth (Bi) was deposited on the Sb film using the same evaporation system to form a multilayer structure. The thickness of Bi film was 150 nm.

Measurements included transmission spectrum, current-voltage characteristics, Seeback effect and temperature-dependent resistance. The samples were thermally annealed in room environment using 120 W tungsten lamp. The measurements were performed on the annealed samples to explain the effect of thermal annealing on the characteristics of such structures.

III. RESULTS AND DISCUSSION

As shown in Fig. 1, the transmittance of both films (bismuth and antimony) is decreased as the incident wavelength is increased within the range (300-900) nm. The maximum transmittance is about 50% at 400 nm while it decreases to 25% for bismuth film and 15% for antimony film at 900 nm. This assigns that Sb thin films absorb in the near-infrared (NIR) region higher than in the visible region. Hence, the compound semiconductors containing this element (AlSb, InSb, GaSb) are employed in efficient infrared detectors due to their narrow bandgaps. Although all elements of V group (N, P, As, Sb, Bi) has the same configuration in the last orbital ($\#s^2\ \#p^3$), bismuth ($6s^2\ 6p^3$) rarely behaves as an individual semiconductor.

Fig. 2 shows the transmittance of the 300 nm Bi/Sb structure within the same range of wavelengths (300-900) nm before and after thermal annealing process at 500 °C. It is clear that the transmittance of the Bi/Sb structure is decreased to 50% of its maximum in case of individual films. This is definitely attributed to the increasing in film thickness (300 nm), which causes to increase the absorption of the incident photon energy. This transmittance is decreased by 20% after annealing because the bismuth atoms diffused in the antimony lattice and fill any available vacancies. The formed structure absorbs more than 97% of the incident photon energy at wavelength longer than 900 nm. This may encourage examining this structures in NIR photodetectors.

In order to introduce the type of conductivity of the Bi-Sb structure annealed at 180 °C, Seeback coefficient was determined as a function of temperature and plotted in Fig. 3. As the slope is negative within (30-70 °C), then the Bi-Sb is an n-type semiconductor. The slope converts to be positive at higher temperatures. This can be interpreted as follows: the excess heating causes electrons to release from the conduction band then other electrons translate from covalence to conduction band then release too. As electrons continue to leave conduction band, the holes in the covalence band are being the majority carriers and the semiconductor begins to behave as a p-type material. Temperature of 500 °C may be considered low to induce such variations in type of conductivity in bulk semiconductors, but in case of thin films, such temperatures corresponding to about 0.066 eV are enough to induce such variations.

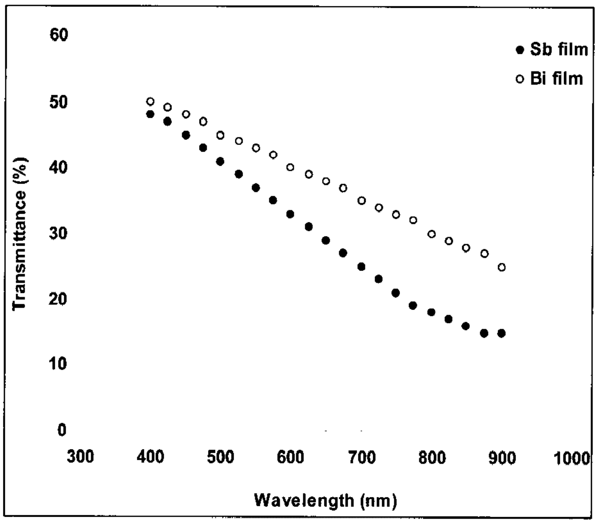


Fig. 1. Transmittance of Sb and Bi thin films versus the incident wavelength.

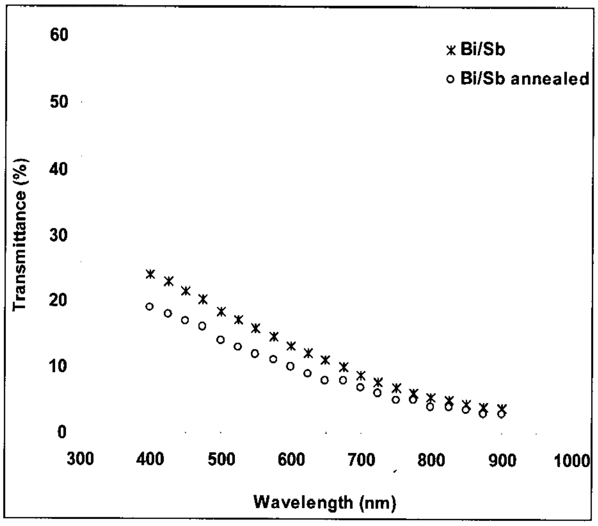


Fig. 2. Transmittance of Bi/Sb thin film structure versus the incident wavelength before and after thermal annealing at 500 °C.

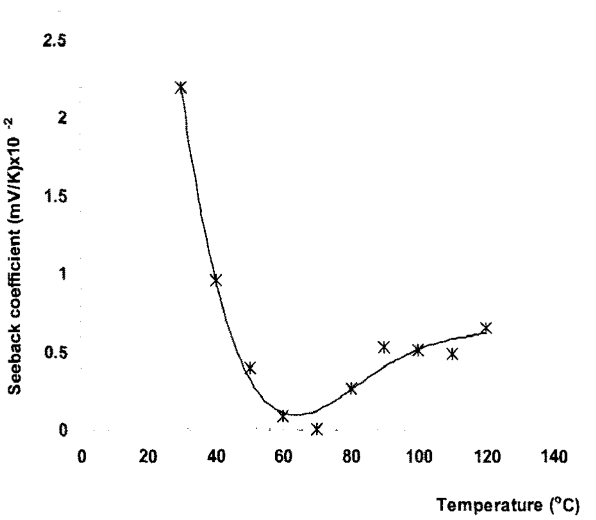


Fig. 3. Seeback coefficient as a function of temperature for the Bi-Sb structure thermally annealed at 500 °C.

The bulk resistance of the Bi-Sb structure was determined as a function of temperature before and after annealing. As shown in Fig. 4, the resistance decreased with increasing substrate temperature, which is attributed to the elimination or at least reduction of the frozen-in defects in Bi-Sb structure. Also, the thermal annealing caused to increase the resistance because it provided energy for much bonding through the outer shield electrons in bismuth and antimony. Hence, the contribution of charge carriers in conduction, and hence the conductivity, is decreased then the resistivity of the structure is increased. In order to determine the reason for variation in the resistivity of the Bi-Sb structure after annealing, the variation of (log R) with ($1/T$) was plotted in Fig. 5. As the relation is exponential then the variation of the resistivity is solely due to the variation of carrier concentration.

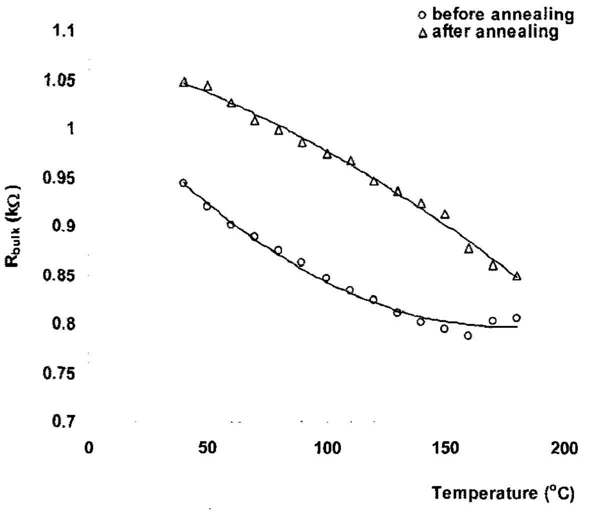


Fig. 4. Bulk resistance of the Bi-Sb thin film structure as a function of temperature before and after annealing.

The I-V characteristics are the most common to introduce the variations in electrical properties of semiconductors. Hence, the I-V characteristics at different temperatures were shown in Fig. 6 for the prepared samples before annealing process. It is clear that increasing temperature caused to increase the current resulted from applying voltage on the structure. There are two possibilities for the electrical properties of the Bi-Sb structure. The first is that bismuth film acts as metal, then increasing temperature induces Bi atoms to diffuse in the Sb lattice and improve electrical conductivity. The second is that the bismuth acts as semiconductor, then the Bi-Sb struc-

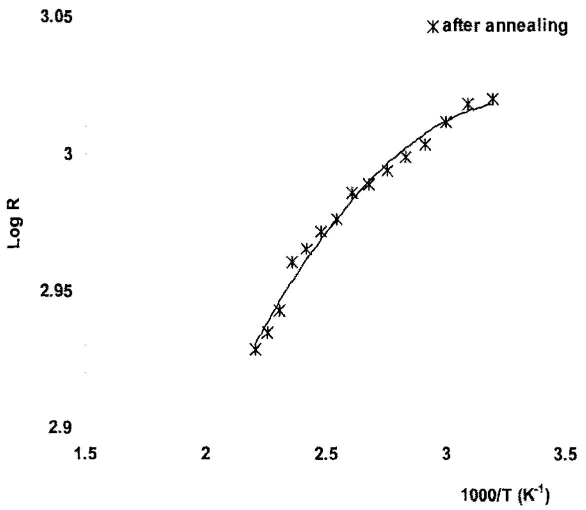


Fig. 5. Log R versus $1/T$ for Bi-Sb structure after annealing.

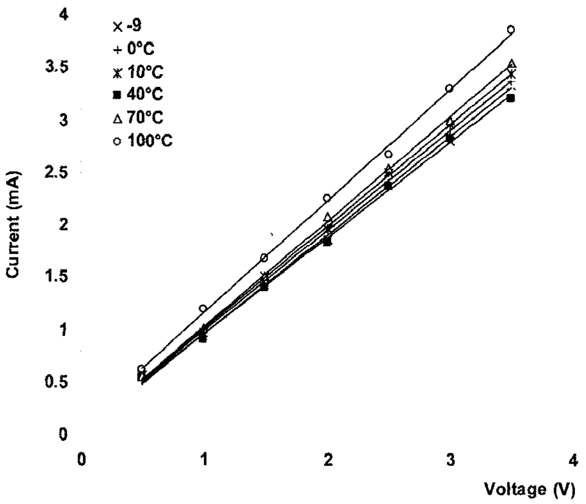


Fig. 6. The I-V characteristics of the Bi-Sb thin film structure at different temperatures before annealing.

ture is a homojunction and its electrical properties are mainly dependent on temperature and the availability of charge carriers is enhanced with increasing temperature.

After annealing the Bi-Sb structure at 500 °C, the I-V characteristics were introduced and shown in Fig. 7. At temperature of 0 °C, the current was increased by 30% after annealing while it was increased by 40% at 100 °C. Thermal annealing affects the diffusion and bonding configurations between Bi and Sb atoms towards better electrical characteristics.

As the electrical properties are affected by thermal annealing, the surface morphology is also affected. Fig. 8 shows the microscopy of the Sb and Bi films and the Bi-Sb samples before and after annealing. The morphology of Sb and Bi films individually is homogeneous while that of Bi-Sb structure is completely different in case of annealing. Also, thermal annealing at 500 °C causes to form hexagonal adjacent islands of 850 μm in width. The formation of such islands is attributed to the temperature-dependent bonding of Bi and Sb atoms. This uniform structure can be considered as an improvement in the morphology.

IV. CONCLUSIONS

Due to the obtained results, thermal annealing at temperatures of 500 °C may enhance the electrical and structural properties of the Bi-Sb thin film structure prepared by thermal evaporation method. The optical

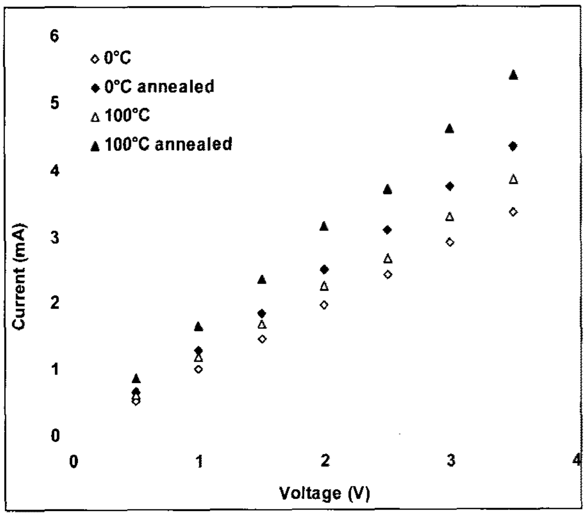
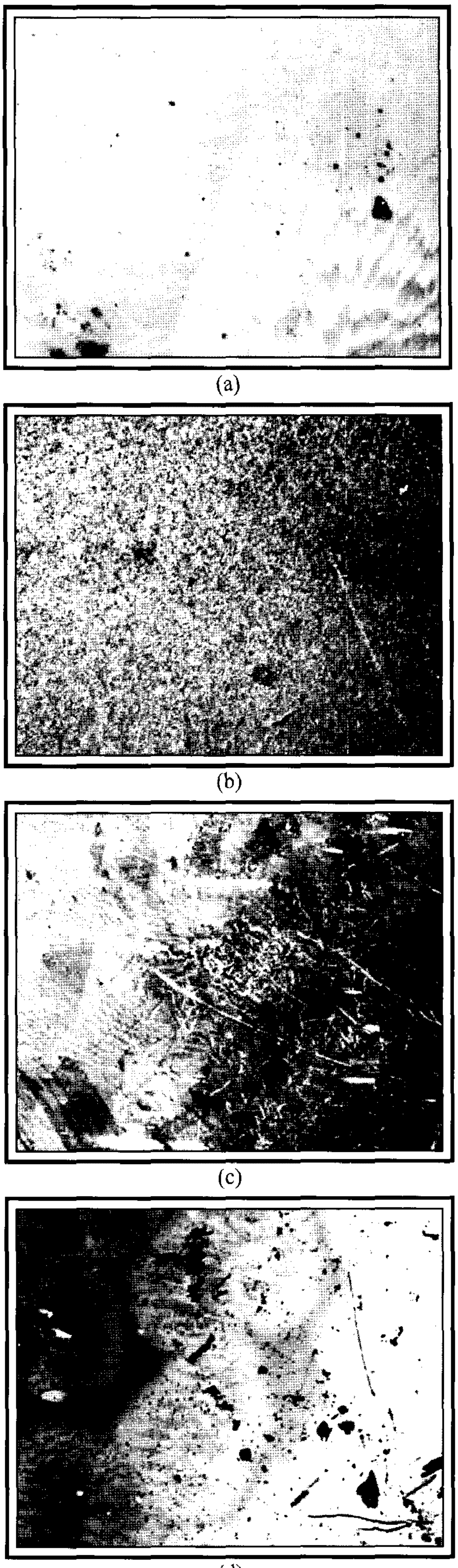


Fig. 7. The I-V characteristics of the Bi-Sb thin film structure at two different temperatures (0 °C and 100 °C) after annealing at 500 °C.



(a)

(b)

(c)

(d)

Fig. 8. The morphology of (a) Sb film, (b) Bi film, (c) Bi-Sb structure annealed at 100 °C and (d) Bi-Sb structure annealed at 500 °C (x20).

properties of such structures are also affected by the thermal annealing because it improves the absorption of the incident photon energy to reach about 97% in NIR region. The obtained results confirmed that the variation in electrical resistivity of the Bi-Sb structure is due to variation of carrier concentration. The prepared samples can be employed in several applications, such as photodetectors, LED's and optical switches.

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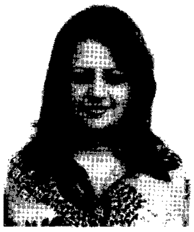

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