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Characterization of Bi incorporated Sb_2Se_3 thin films deposited by arrested precipitation technique

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Abstract

Antimony bismuth selenide thin films ($Sb_{2-x}Bi_xSe_3$), with x varying from 0.00 to 0.10, have been deposited on glass substrate using the arrested precipitation technique (APT). The preparative parameters such as temperature, concentration, and pH have been optimized in order to deposit $Sb_{2-x}Bi_xSe_3$ thin films. The as-deposited $Sb_{2-x}Bi_xSe_3$ thin films are specularly reflective and orange in colour. The films were characterized by optical absorption, x-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive x-ray analysis (EDS) studies. An analysis of the optical absorption data of the as-deposited films revealed an indirect transition with the estimation of the corresponding band gap value.

Keywords: Arrested precipitate technique; Thin film; Optical; Structural; EDS

1. Introduction

Ternary and multinary amorphous chalcogenide films are very promising materials because their diverse active properties allow their application as in infrared optical fibers, reversible phase change optical records, xerography, photolithography and optical memories [1,2]. Antimony and bismuth selenide based materials owing to its good photoconductive properties and high thermoelectric power has wide applications to optical devices and thermoelectric cooling devices [3-6]. In general, the chalcogenide thin films of antimony and bismuth based materials are fabricated by chemical or physical vapour deposition [7, 8]. Compared to these techniques, the arrested precipitation technique may offer a low synthesis temperature, simple and low cost growth method for photoconductive and thermoelectric materials in laboratory atmosphere. The most advantageous point of arrested precipitation technique is that the doping concentration can be easily controlled through adjusting the parameters of the process. The purpose of the present work is to study composition dependence of the optical energy gap of the investigated films in the $Sb_{2-x}Bi_xSe_3$ system ($0 \leq x \leq 1$ at %). The composition dependence of the optical energy gap of the investigated films is discussed on the basis of the concentration of covalent bonds formed in the chalcogenide thin film. Knowledge of the optical properties of these amorphous materials is obviously necessary for exploiting their very interesting technological potential.

2. Experimental details

2.1. Deposition of the $Sb_{2-x}Bi_xSe_3$

$Sb_{2-x}Bi_xSe_3$ thin films were produced by the arrested precipitation technique on glass substrates. The substrate used for deposition of $Sb_{2-x}Bi_xSe_3$ thin films were glass slides with the size of 75 mm x 25 mm x 1.3 mm. The substrates were washed well with alkaline soap solution and then boiled in double distilled water for 10 minutes. The proposed solution growth technique is very simple and does not require any special set-up. It is based on a hydrolysis of sodium

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selenosulphite to Se^- and slow dissociation of complex ions. The reaction rate was controlled through the bath temperature, the solution pH and the relative concentration of the reactants in the deposition bath. The solution of sodium selenosulphite was prepared by refluxing selenium metal powder and sodium sulphite solution for about 6 hours at 70 ℃. To prevent the hydrolysis of bismuth nitrate and antimony trichloride, $Bi(NO_3)_35H_2O$ was dissolved in triethanolamine and $SbCl_3$ was dissolved in tartaric acid. Bi doping was achieved by the introduction of appropriate amount of Bi –TEA. The bath composition found to be suitable for deposition of $Sb_{1.98}Bi_{0.02}Se_3$ thin films was: 19.8 ml 0.30 M Sb tartarate and 0.2 ml 0.30 M Bi-TEA is taken in 100 ml beaker. 30% NH_4OH is added drop wise to obtain alkaline media of pH 10.5. Then 30 ml 0.30 M Na_2SeSO_3 solution is introduced into the beaker and rest is water to make total volume 70 ml. Substrates are fixed to a specially designed substrate holder and mounted vertically in the bath at 20 ± 0.5 ℃. An orange precipitates gradually fills the bath and turns brown after 1 hour. During deposition period beaker was kept undisturbed.

After deposition glass substrate were removed from the deposition bath, washed in double distilled water and kept in dark desiccators. The $Sb_{2-x}Bi_xSe_3$ thin films deposited on the glass slides were orange brown in colours.

2.2. Post-deposition characterization

The composition, structure, morphology and optical characteristics of the as deposited $Sb_{2-x}Bi_xSe_3$ samples have been analysed as a function of bismuth concentration (x). The microstructure of the films was examined using a high-resolution scanning electron microscope (SEM), which is combined with an electron microprobe analyzer to measure relative concentration of the elements with an accuracy of ± 2%. A JEOL-JSM- 6360A scanning electron microscope with an energy dispersive x-ray analysis (EDS) attachment is used to record scanning electron microscopy (SEM) micrograph and EDS spectrum of the samples. The amorphous nature was confirmed by the absence of peaks in the X-ray diffractograms of thin films. The optical absorption spectrum was recorded at room temperature using a UV-visible spectrophotometer (Hitachi model 330, Japan) in the wavelength interval of 350-850 nm. To enable the optical absorption, the films grown on back side were removed by cotton swabs dipped in concentrated HCl. A clean glass substrate identical to the coated substrate was used as reference. The X-ray diffraction analysis was carried out for all as-deposited films using a Philips PW-1710 X-ray diffractometer for the 2θ ranging from 20^0 to 100^0 with CuK_α line used as a beam (λ=1.5418A^0).

3. Results and discussion

3.1. Deposition of the films

3.1.1. Growth mechanism of $Sb_{2-x}Bi_xSe_3$ thin films

The $Sb_{2-x}Bi_xSe_3$ thin films can be obtained from an aqueous bath containing antimony and bismuth salt in complex form, and selenide ions. The deposition process based on release of Sb^{3+}, Bi^{3+} and Se^{2-} ions in the solution which then condense ion by ion process on the substrate materials. In the present case, ionic species of Bi^{3+}, Sb^{3+} and Se^{2-} are produced as per the following reaction equilibria in an aqueous alkaline deposition bath.

$$SbCl_3 + 3C_4H_6O_6 + 3NH_4OH \longrightarrow (NH_4)_3[Sb(TA)_3] + 3HCl + 3H_2O$$

Tartaric acid

$$(NH_4)_3[Sb(TA)_3] + 6H_2O \longrightarrow Sb^{3+} + 3TA + 3NH_4OH + 3OH^- \quad \text{.....(1)}$$

$$(NH_4)_3[Bi\ 2N(CH_2\text{-}CH_2\text{-}O)_3] + 6\,H_2O \longrightarrow Bi^{3+} + 3NH_4OH + 3\ OH^- +$$

$$2\,[N(CH_2\text{-}CH_2\text{-}OH)_3] \text{ ..... (2)}$$

$$Na_2SeSO_3 + OH^- \longrightarrow Na_2SO_4 + HSe^-$$

$$HSe^- + OH^- \longrightarrow H_2O + Se^{2-} \text{ ..... (3)}$$

The reactions (1) and (2) shows that the metal ions are produced by dissociation of the metal complex while chalcogen ions are produced by dissociation of sodium selenosulphite.

$$Sb_{2-x}^{3+} + Bi_x^{3+} + 3\,Se^{2-} \longrightarrow Sb_{2-x}Bi_xSe_3 \quad \text{..... (4)}$$

From the reaction (4), it is revealed that ion by ion condensation of Sb^{3+}, Bi^{3+} and Se^{2-} results in the formation of $Sb_{2-x}Bi_xSe_3$ thin film on substrate.

3.1.2. Growth kinetics of the thin film formation

In arrested precipitation technique, a complexing agent is used to bind the metallic ions to avoid the homogeneous precipitation of the corresponding compound. The formation of complex ion is essential to control the rate of reaction and to avoid the immediate precipitation of compound in the solution. The metal complex hydrolyses slowly to generate the positive ions in solution. A solution, containing the metal complexes, was mixed with a solution which produces negative ions by hydrolyses. When the solution is saturated, the ionic product is equal to the solubility product and when it exceeds, ions combines on the substrate to form the nuclei. It is known that entire process passes through nucleation phase, growth phase and a terminal phase [13]. The presence of the surface of a substrate introduces a degree of homogeneity that facilitates nucleation in film growth processes. Therefore, the surface of the substrate can be considered a catalyst activating the nucleation. Once nucleation has begun on a substrate, it generally becomes easier for the film to grow, since deposition usually occurs more easily on the nucleated surface than on the clean surface. Either homogeneous or heterogeneous deposition can occur. The homogeneous process is the faster one, resulting in the adsorption of powdery particles on the substrate due to the bulk precipitation. So, the formation of metal complex is essential to minimise the homogeneous process. In the heterogeneous process, the preferential adsorption of Bi^{3+}, Sb^{3+} and Se^{2-} ions will take place, leading to the uniform nucleation and growth of the thin film.

Na_2SeSO_3 was prepared by refluxing selenium metal powder and excess of sodium sulphite solution. The excess concentration of sodium sulphite prevents oxidation of selenide and its reprecipitation as selenium [14].

Addition of NH_4OH increases the OH^- ion concentration in the solution and thereby favours the hydrolysis of the chalcogen precursor.

3.2. Optical Studies

The optical absorption coefficient of $Sb_{2-x}Bi_xSe_3$ with different composition was calculated using the absorbance value measured for a particular wavelength (λ) and film thickness (t) using the relation

$$\text{Absorption Coefficient } (\alpha) = \text{Optical density/Thickness } (t)$$

Thickness of the film was calculated by assuming density of the film is equal to bulk material and using the relation

$$t = M / A \times d$$

Where 'M' is the mass of the thin film deposited on the substrate, 'A' is area of the film and'd' is density of the bulk material.

The optical band gap will be found from the calculated values of the absorption coefficient (α). The dependence of the optical absorption on the photon energy is described by the relation [14]

$$(\alpha\, h\, \nu)^{1/n} = A(h\, \nu - E_g) \quad \text{---------(1)}$$

where 'h' is Planck's constant, 'ν' is frequency, 'A' is parameter that depends on the transition probability and 'E_g' is the optical energy gap of the investigated sample and exponent 'n' depends on the type of transition. For direct allowed n=1/2, indirect allowed transition n=2, and for direct forbidden n=3/2. The values of the optical band gap have been calculated from the best straight line fits in '$(\alpha\, h\, \nu)^{1/n}$' versus 'h ν' plots and corresponding band gaps were obtained from extrapolating the straight portion of the graph on 'h ν' axis at α = 0.

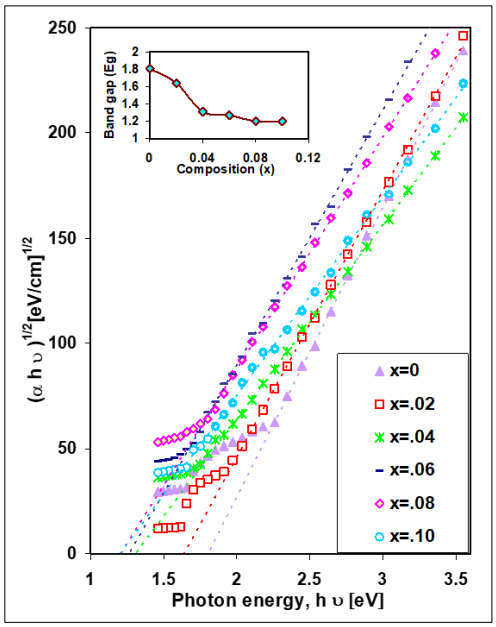

Figure 1 The $(\alpha h\nu)^{1/2}$ vs. hν plots for the $Sb_{2-x}Bi_xSe_3$ films having different composition, inset: variation of optical band gap with Bi content

The mode of optical transition has also been determined by plotting ln (α h ν) versus ln (h ν -E_g) [15].

Equation (1) is

$$(\alpha h \nu)^{1/n} = A(h \nu - E_g)$$

$$(\alpha h \nu) = A(h \nu - E_g)^n$$

$$\ln (\alpha h \nu) = \ln A + n \ln (h \nu - E_g)$$

For direct allowed type of transition n=0.5 and for indirect allowed type of transition n=2. Thus the plot of ln (α h ν) versus ln (h ν-E_g) yields a straight line whose slope is equal to 2 for $Sb_{2-x}Bi_xSe_3$ confirming indirect allowed type of transition (Fig.2).

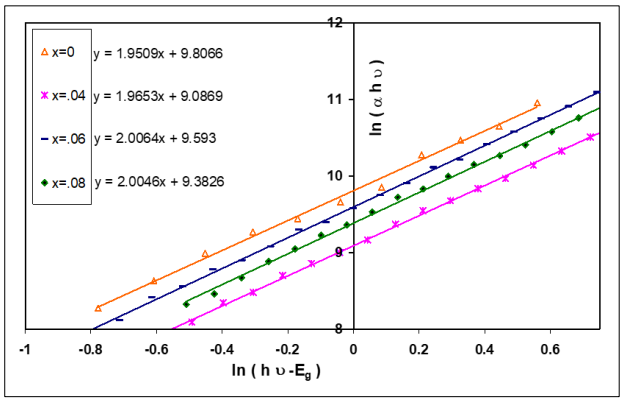

Figure 2 Evolution of the mode of transition from the variation of ln (α h ν) versus ln (h ν-Eg) for $Sb_{2-x}Bi_xSe_3$ samples

The values of slopes obtained from ln (α h ν) versus ln (h ν-E_g) plots are listed in Table 1

Table 1 Optical energy gap and power factor of as-deposited $Sb_{2-x}Bi_xSe_3$ films

Sb_2-xBixSe_3 Film Composition (x)	**Band gap (Eg)**	**Power factor (slope) (n)**
0.0	1.81	1.9509
0.02	1.64	-------
0.04	1.31	1.9653
0.06	1.27	2.0064
0.08	1.20	2.0046
0.10	1.20	--------

The optical absorption coefficient is found to be order of 10^4 cm^{-1} for $Sb_{2-x}Bi_xSe_3$ films respectively. Optical absorbance measurements of the films were used to estimate the band gap energy and it was found to change with alloy composition 'x' in $Sb_{2-x}Bi_xSe_3$ thin films. As the value of Bi content in the film (x) increases, the band gap is shifted to lower values and band gap tailoring is achieved in the alloy film. The transition type of Sb_2Se_3 is matter of discussion in the literature. We are assuming indirect transition type as the linearity of '$(\alpha h \nu)^{1/2}$' versus 'h ν' (Fig. 1) is more evident compared to the '$(\alpha h \nu)^{2}$' versus 'h ν' plot for direct allowed transition types. We do not observe a straight line behaviour on graphs of '$(\alpha h \nu)^{2/3}$' versus 'h ν' (direct forbidden), '$(\alpha h \nu)^{1/3}$' versus 'h ν' (Indirect forbidden), '$(\alpha h \nu)^{2}$' versus 'h ν'(direct allowed). These plots (not shown) reveal that the type of transition is neither direct / indirect forbidden nor direct allowed. Fig. 1 is a typical best fit of '$(\alpha h \nu)^{1/2}$' versus 'h ν' for six different composition and the values of the optical band gap E_g were taken as the intercept of '$(\alpha h \nu)^{1/2}$' versus 'h ν' at '$(\alpha h \nu)^{1/2}$' = 0. The estimated values of E_g of different composition $Sb_{2-x}Bi_xSe_3$ films are listed in table 1. The variation of band gap energy with Bi content is shown in the inset of figure 2. The substitution of 'Sb' atoms by 'Bi' atoms in amorphous $Sb_{2-x}Bi_xSe_3$ thin films results in decreasing the optical band gap of the system and finally reaches a steady value. The decrease in band gap is caused by alloying effect. This effect causes changes in bond angles and/or bond lengths [16]. The same observation was found by M. M. El-Samanoudy for replacement of Sb atoms by Bi atoms in case of $Ge_{25}Sb_{15-x}Bi_xS_{60}$thin films [17].

The decrease in optical energy gap with increasing Bi content can be explained on the basis of chemical bond approach [18, 19]. The assumptions used for chemical bond approach are i) Atoms combine more favourably with atoms of different kinds than with the same kind. Bonds between like atoms will occur only if there is an excess of certain type of atom. ii) Bonds are formed in the sequence of decreasing bond energy iii) each constituent atom is coordinated by 8-N atoms, where N is number of outer shell electrons and this is equivalent to neglecting the dangling bonds and the outer valence defects. The bond energies for Se-Se, Sb-Se, Sb-Sb, Bi-Bi and Bi-Se bonds are 44.0, 42.9, 30.2, 25.0 and 40.7 Kcal/mole respectively [20]. When chemical bond approach is applied to Sb_2Se_3 specimen, it is expected that only Se-Se and Sb-Se bonds would be present. When Bi is incorporated into the matrix, Bi is expected to bond preferably with Se and not to Sb. Since Sb-Se bond has the largest bond energy value, therefore it is expected that Se atoms would completely saturate the valences of the Bi atoms. Therefore Sb-Bi, Sb-Sb, and Bi-Bi bonds are not expected to form in this composition. Thus the addition of Bi atom in Sb_2Se_3 leads to the formation of Bi-Se bonds at the expense of Se-Se bonds. Thus the number of Bi-Se bonds increases and average bond energy of the compound decrease; hence the optical energy decreases with increasing Bi content.

3.3. XRD studies

The structure of the films was studied from the XRD pattern (figure 5) which reveals that the as-prepared $Sb_{2-x}Bi_xSe_3$ films are amorphous in nature. X-ray diffraction pattern of the as deposited thin films have been measured to ascertain the non-crystalline nature of the material. The presence of only broad features and the absence of any sharp peaks in the diffractograms are taken as evidence for the amorphous nature of the thin film samples. An amorphous structure is expected since deposition is carried out at low temperature (20 °C).

3.4. SEM / EDS

The morphology of these films was analysed in order to obtain a higher rate of grain nucleation and a more refined grain structure. SEM photographs in the figure 3 were taken at 20,000 X magnification to observe the surface morphology. No pin holes or cracks could be observed for all the samples. The grains shows agglomerated morphology and appear very homogeneous. The figure shows compact structure composed of single type small densely packed crystals. The SEM shows increase in number of grains with increase in x which is confirmed from increase in film thickness. The surface of the substrate was not covered completely upto X= 0.06.

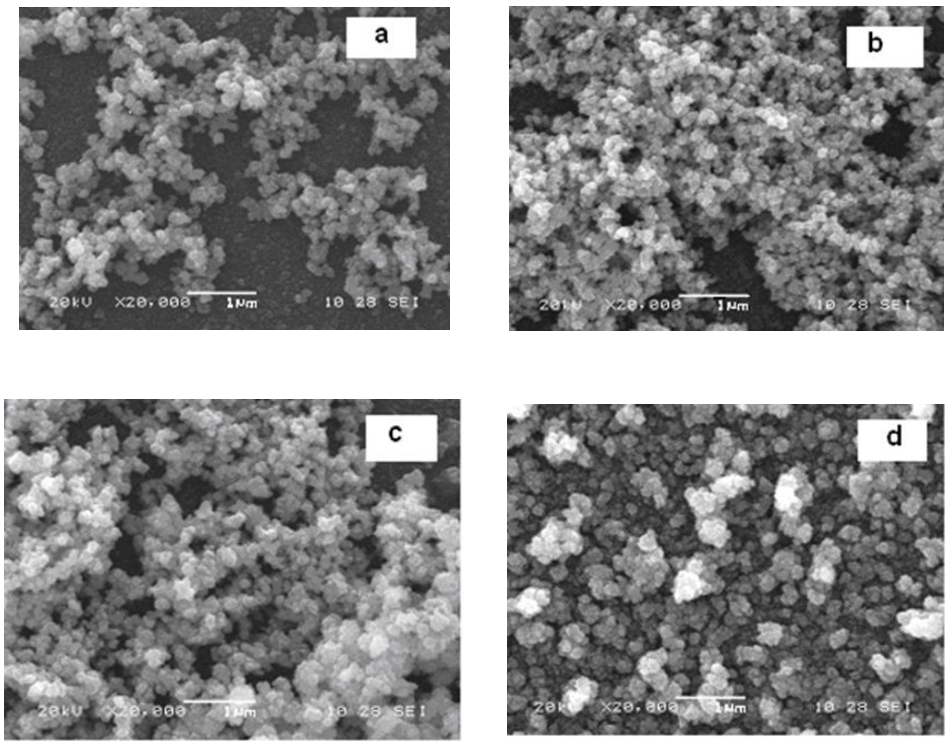

Figure 3 SEM micrographs for $Sb_{2-x}Bi_xSe_3$ films : (a) x=0.04 (b) x= 0.06 (c) x=0.08 (d) x=0.10

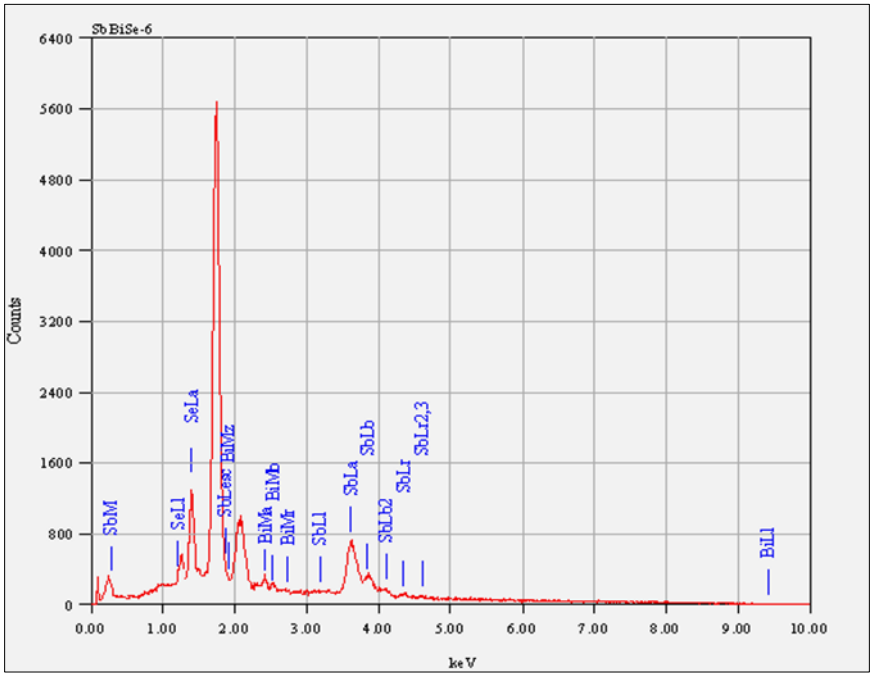

Figure 4 The EDS scanning pattern of the typical as-deposited $Sb_{1.90}Bi_{0.10}Se_3$ thin film

Compositional analysis was carried out by EDS analysis. A typical EDS spectrum is shown in figure 4. The average atomic percentage ratio of Se/Sb+Bi, gives the value of 0.66, 0.67, 0.69, 0.69 for different Bi contents (x) 0, 0.02, 0.06 and 0.10 respectively. The observed atomic percentage ratios of Se/Sb+Bi of the films are less than the stoichiometric ratio (1.5). Deviation from the atomic percentages of Se/Sb+Bi could be attributed to the incorporation oxygen from the

atmosphere or from the alkaline medium of the bath solution. The excess of Sb is bounded to oxygen in the form of $Sb(OH)_3$ and Sb_2O_3. The dopant (Bi) concentration in the starting solution was varied from 0.4% to 2.0%. But actually dopant concentration 0.34 to 1.93 % was observed in the film as evident from the EDS analysis and summarized in Table 2.

Table 2 EDS analysis of the as-deposited $Sb_{2-x}Bi_xSe_3$ thin films

Film Composition	Elements (Expected at %)			Elements (Actual at %)		
	Sb	Bi	Se	Sb	Bi	Se
Sb_2Se_3	40.00	00	60.00	60.19	00	39.81
$Sb_{1.98}$ Bi.02Se_3	39.60	0.4	60.00	59.54	0.34	40.12
$Sb_{1.94}$ Bi.06Se_3	38.80	1.20	60.00	58.22	1.12	40.66
$Sb_{1.90}$ $Bi_{0.1}Se_3$	38.00	2.00	60.00	57.37	1.93	40.70

4. Conclusion

APT deposited $Sb_{2-x}Bi_xSe_3$ films on glass substrates had good adherence and were free of pinholes. The growth kinetics, morphology and optical gap of the $Sb_{2-x}Bi_xSe_3$ films were modified with increase in bismuth content. The grain size of the layers increases and becomes more uniform with Bi content. Thus Bi atoms serve as additional nucleation centers. The optical absorption measurements for $Sb_{2-x}Bi_xSe_3$ films indicate that the absorption mechanism is due to indirect transition. The rate the change of the optical gap decreases with increasing Bi content.

Compliance with ethical standards

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Disclosure of conflict of interest

The author declares no conflict of interest.

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