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Formation Process of MnBi Thin Films by Williams' Method

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Williams has found that when Mn and Bi are successively evaporated on a glass substrate, followed by prolonged annealing around 300 °C, a ferromagnetic MnBi thin film can be obtained with its *c*-axis perpendicular to the film plane. In order to elucidate the formation process of the film, Rutherford backscattering (RBS) experiment, X-ray diffractometry, electron microscope study, and magnetic measurement are carried out. It is found that at the first stage of annealing up to 250 °C a non-magnetic transitional compound $Mn_{1.2}Bi$ is formed, and during the subsequent annealing at 250 °C, the final MnBi crystals with the aligned *c*-axes nucleate, and grow at the expense of the transitional phase. It seems likely that at the last stage of reaction, a few Bi crystals remaining in the transitional phase may serve as the nuclei.

Williams hat gefunden, daß durch sukzessives Aufdampfen von Mn und Bi auf ein Glassubstrat sowie nachfolgender ausgedehnter Temperung bei 300 °C eine ferromagnetische MnBi-Schicht erhalten wird, deren *c*-Achse senkrecht zur Schichtebene ist. Um den Bildungsprozeß der Schicht aufzudecken, werden Rutherford-Rückstreu-Experimente (RBS), Röntgendiffraktometrie, Elektronenmikroskopieanalysen und magnetische Messungen durchgeführt. Es wird gefunden, daß bei der ersten Ausheilstufe bis 250 °C eine nichtmagnetische Übergangsverbindung $Mn_{1,2}Bi$ gebildet wird und während der nachfolgenden Temperung bei 250 °C die endgültigen MnBi-Kristalle mit ausgerichteter *c*-Achse gebildet werden und auf Kosten der Übergangsphase wachsen. Es scheint wahrscheinlich, daß bei den letzten Reaktionsstufen einige Bi-Kristalle, die in der Übergangsphase zurückbleiben, als Keime wirken können.

1. Introduction

A ferromagnetic MnBi thin film with the easy axis perpendicular to the film plane was first prepared by Williams et al. [1]. According to this method, when nearly equiatomic amounts of Mn and Bi were successively evaporated on a glass substrate, followed by annealing around 300 °C for three days, a MnBi thin film could be obtained. It has been noticed that the thin film thus obtained possesses a prominent texture in which its *c*-axis is aligned normal to the film plane, capable of applying to a perpendicular magnetic recording. Afterwards, Chen found another method of preparing a similar MnBi thin film, in which Bi and Mn were evaporated in the reverse order [2]. When the double layer film is annealed at 300 °C, we can obtain a well-orientated MnBi film in a very short period of time. Iwama et al. [3] have investigated the formation process by Chen's method, to elucidate that the Bi film firstly evaporated has a texture in which its trigonal *c*-axis perpendicular to the substrate, and during annealing up to 300 °C, Mn atoms preferentially diffuse into the Bi layer to form MnBi crystals with their *c*-axes aligned. In Williams' method, however, the Bi layer deposited on the Mn layer has no texture, though the method enables one to prepare a similar well-textured MnBi thin film. In the present work, therefore, the formation process of MnBi thin films by Williams' method will be investigated in detail.

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2. Experimental Procedure

Mn and Bi were subsequently evaporated in a vacuum of 10^{-4} Pa on a quartz substrate to prepare a double layer thin film. The atom ratio of Mn to Bi in the specimen, which will be denoted by γ hereafter, was changed from 0.7 to 1.8. After silicon monoxide was evaporated on the specimen surface as a protective layer, it was heated in a vacuum chamber up to 250 °C at a rate of 10 K/min, and then kept at 250 °C in various periods of time.

In order to investigate the behaviour of atomic migration in the film specimen, Rutherford backscattering (RBS) technique was employed. In the experiment helium ions with energy of 1.5 MeV collimated through a slit system were allowed to hit normally the specimen surface of 0.5 mm^2 in area. The backscattered ions were detected by a semiconducting detector set at an angle of 145° with respect to the incident direction. The detector signals were converted through a pulse height analyser into an energy spectrum of the backscattered ions.

The phase constituents involved in the specimen were examined by a conventional X-ray diffractometer using CuK_α radiation, as well as by a transmission electron microscope. In addition, the saturation magnetic moment of the film specimen was measured at room temperature by a vibrating sample magnetometer.

3. Experimental Results and Discussion

As described in many review articles [4], the RBS experiment is very useful in determining the atomic concentration profile in the depth direction of the thin film specimen. Fig. 1 shows RBS energy spectra obtained for double layer films of 96 nm Bi on 37 nm Mn, for which the γ-value is 1.1. For specimens annealed at various temperatures up to 250 °C, each spectrum consists of two distinct parts; the Mn spectrum on the lower-energy side and the Bi one in the higher-energy side. They represent the depth distributions of the respective elements in the specimens. In particular, the Mn spectrum for the as-evaporated specimen (drawn by a broken line) has a low step in the right side, which suggests that a small amount of Mn has already diffused into the Bi layer. As the annealing temperature increases the step becomes higher and higher until at 250 °C the Mn spectrum forms a flat plateau. In this stage, on the other hand, the Bi spectrum of plateau shape gradually decreases in height but increases in width. These results obviously show that Mn diffuses so fast into the Bi

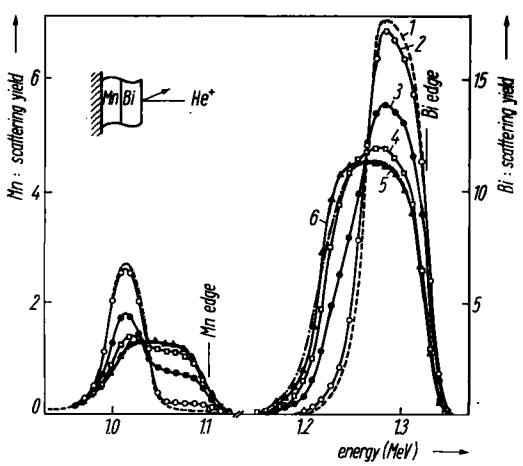


Fig. 1. Backscattering energy spectra ($\times 10^3$) for the 96 nm Bi on 37 nm Mn specimens, (1) as-evaporated, (2) quenched from 180, (3) 200, (4) 220, (5) 250, and (6) annealed at 250 °C for 4 h

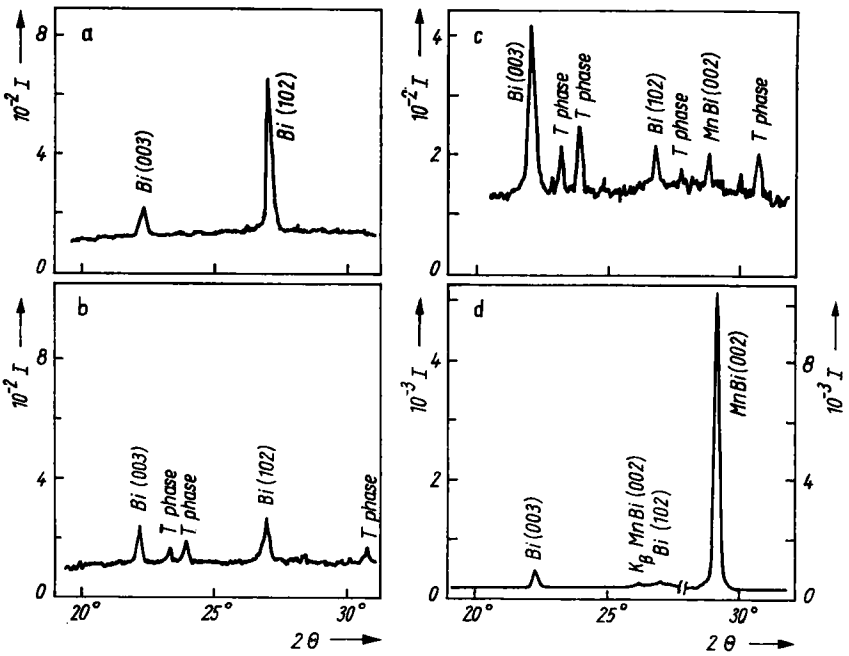


Fig. 2. Intensity I of X-ray diffraction patterns with $\gamma = 1.1$, subjected to annealing with various durations. a) As-evaporated, b) $T = 200$, c) 250, d) 250 °C, annealed for 4 h

layer as to complete the mutual diffusion up to 250 °C. Such a situation seems rather similar to that in Chen's method [3].

X-ray diffractometry was made on the same specimens to examine the phase constituents involved. The results obtained are summarized in Fig. 2a to 2d. As seen in Fig. 2a, the as-evaporated specimen exhibits Bi(003) and Bi(102) diffraction lines, of which the intensity ratio is estimated approximately as 1/5. Since the A.S.T.M. cards tell us that the ratio is 1/10 for Bi powder with no texture, the present Bi crystals deposited on the Mn layer must possess a random orientation. In addition, no Mn line can be observed in the diffraction patterns, possibly because Mn atoms can scarcely contribute to the diffraction due to the form factor. In Fig. 2b for 200 °C annealing several different diffraction lines are recognized besides the Bi lines. In Fig. 2c for 250 °C annealing, these new diffraction lines become more distinct, and besides a MnBi(002) line appears. The new diffraction lines have not yet been reported in the Mn–Bi binary system. It may be assumed, therefore, that they are ascribed to a kind of transitional phase occurring in the first step of the reaction. It will be called T-phase hereafter.

In order to determine the crystal structure of the T-phase, a specimen of 85 nm Bi on 54 nm Mn ($\gamma = 1.8$) was prepared and annealed at 250 °C for 4 h, followed by X-ray diffractometry. In Fig. 3 the diffraction pattern is shown consisting of many lines. It can be analysed with the aid of Hull-Davey charts, leading to the conclusion that the T-phase has an orthorhombic structure with $a = 1.49$, $b = 1.20$, and $c = 1.32$ nm.

Referring back to Fig. 2d, if the double layer specimen with $\gamma = 1.1$ is annealed at 250 °C for 4 h, the diffraction lines associated with the T-phase vanish and instead the MnBi(002) line is much enhanced. This suggests that in this stage the T-phase has almost entirely transformed into the hexagonal MnBi phase with its c-axis normal

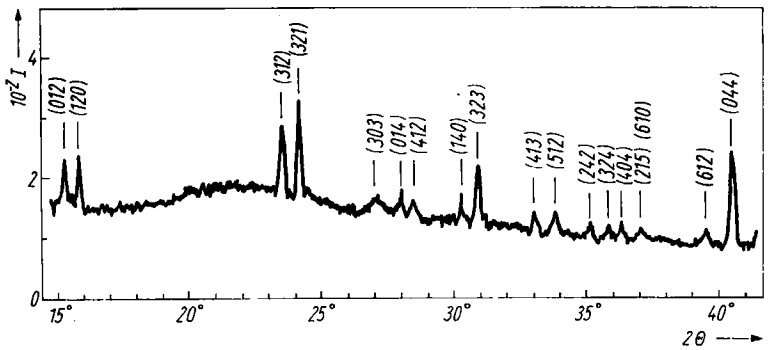


Fig. 3. Intensity I of X-ray diffraction pattern of the T-phase of MnBi (orthorhombic). $a = 1.49$, $b = 1.20$, $c = 1.32$ nm; Mn: 54 nm, Bi: 85 nm

to the film plane. The kinetics of the MnBi formation can be most clearly examined with the measurement of the saturation magnetic moment, because the T-phase is non-magnetic, whereas MnBi is ferromagnetic. Thus, the specimen with an area of 100 mm^2 was annealed at 250 °C for various periods of time, and the magnetic moment was measured at room temperature under a magnetic field applied perpendicular to the film plane. The result obtained is shown in Fig. 4. The time dependence of the magnetic moment may unambiguously represent the reaction kinetics. It is clear that the transformation takes place so fast as to be completed only after about 4 h. The final value of saturation magnetic moment is 1.0×10^{-11} Wb m, which corresponds to 0.75 Wb/m^2 in magnetization per unit volume. It is to be noted that this value is a little lower than the nominal magnetization of MnBi, 0.83 Wb/m^2.

The transition behaviour of the T to MnBi-phase can be observed by means of an optical microscope as shown in Fig. 5a to 5c. The T-phase looks like and under the conventional microscope with low magnification, probably because it is composed of fine crystallites. In fact, Fig. 5a reveals that a sandy matrix of the T-phase covers almost all the surface for the specimen annealed up to 250 °C. On the same specimen, however, a few distinct regions with smooth appearance can be recognized within the sandy matrix. When further annealed at 250 °C for 30 min, the smooth regions, which probably correspond to the final MnBi phase, grow laterally at the expense of the T-phase, as shown in Fig. 5b. Here the remaining T-phase is observed in the upper left side of the photo. After annealing at 250 °C for 4 h, a few, but very large crystals of MnBi are developed covering all the surface. Thus, the final grain size of MnBi may become larger than 1 mm in diameter.

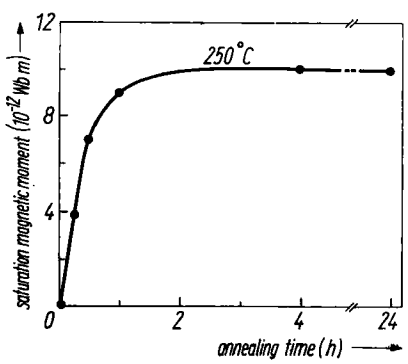
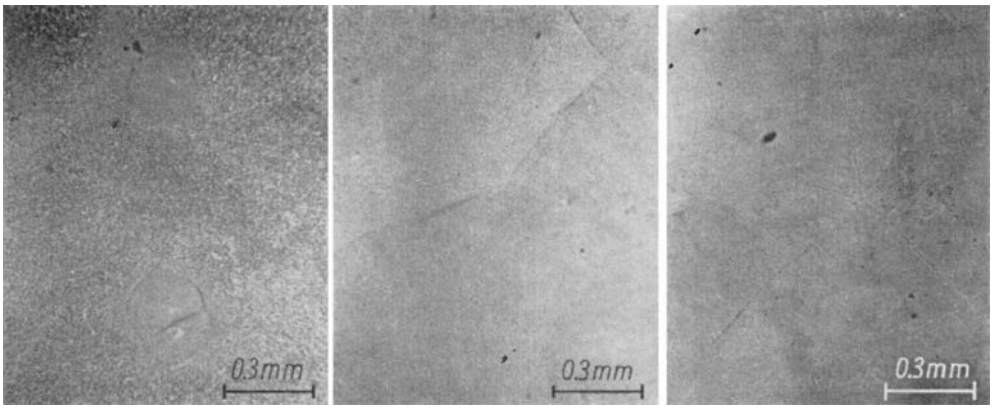


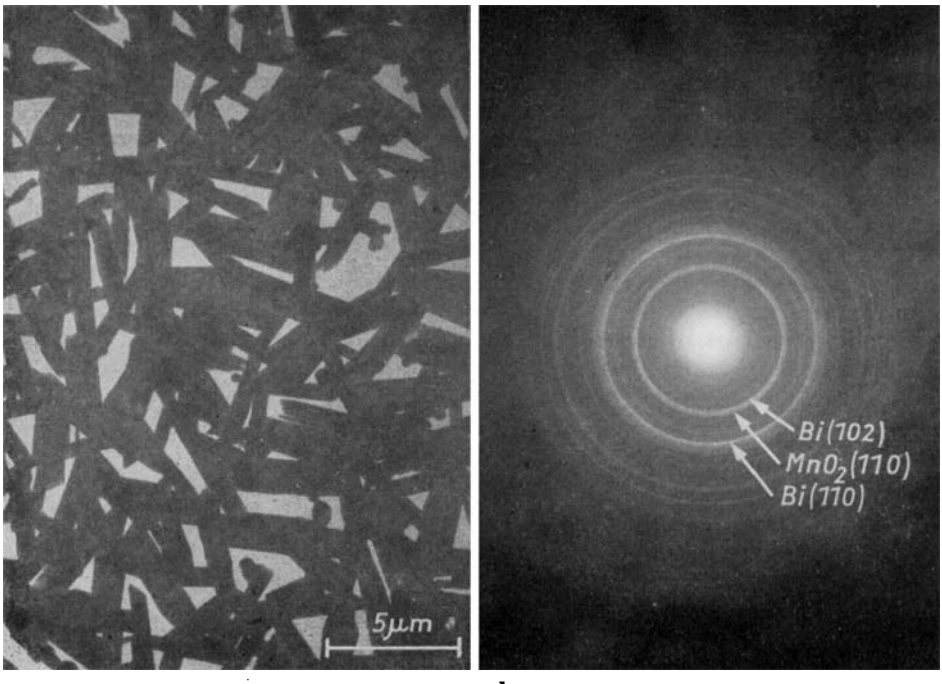
Fig. 4. Changes in saturation magnetic moment with annealing time at 250 °C. $\gamma = 1.1$, Mn: 37 nm, Bi: 96 nm



a b c

Fig. 5. Optical micrographs of specimens, a) quenched from 250 °C, b) annealed at 250 °C for 30 min, and c) annealed at 250 °C for 4 h

Next, in order to investigate the morphology of the T-phase in more detail, a transmission electron microscopic observation was made using a specimen about 50 nm thick. Fig. 6a shows a micrograph obtained for the specimen annealed at 250 °C, followed by quenching. The dark regions occupying a great part of the whole area consist of many rod-like particles about 1 μm wide and 5 μm long. They can be identified as the T-phase from the electron diffraction pattern shown in Fig. 6b, where



a b

Fig. 6. TEM micrograph and electron diffraction pattern of the specimen with 60 nm Bi on 20 nm Mn, annealed at 250 °C

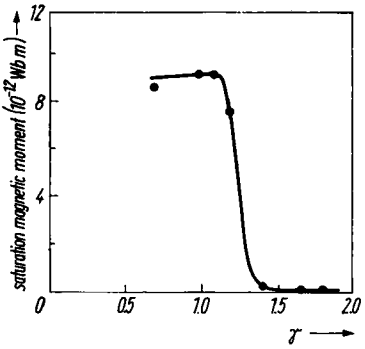


Fig. 7. Changes in saturation magnetic moment with the deposition atom ratio. Mn: 35 nm

one sees many diffraction rings corresponding to those of the T-phase. In addition, there are observed two Bi diffraction rings as well as a MnO_2 ring as denoted by the respective indices. They reveal that some unreacted Bi and Mn have been partially oxidized during annealing.

Now, it has been found that if the Williams type of double layer film is annealed at 250 °C, an unknown non-magnetic compound named the T-phase is formed in the first place, and then the T-phase gradually transforms into the final ferromagnetic MnBi phase during further prolonged annealing. Here it is seemingly a wonder that whereas the T-phase consists of fine crystals perhaps with random orientations, the final MnBi crystals grow with their *c*-axes normal to the film plane. Accordingly, the following experiments have been performed to elucidate the transformation mechanism more closely.

At first, an influence of the specimen composition upon the behaviour of the transformation has been examined. For this purpose, several specimens were prepared in which various thicknesses from 100 to 55 nm of the Bi layer were evaporated on Mn of the constant thickness 35 nm. The atom ratio of Mn to Bi, γ, ranges from 1.0 to 1.8 for these specimens. After being subjected to a prolonged annealing at 250 °C, the saturation magnetic moment was measured. The values obtained for each specimen with the same area of 100 mm^2 is plotted against the γ-value in Fig. 7. It is obviously shown that the magnetic moment is as high as approximately 9.2×10^{-12} Wb m with $\gamma = 1.0$, but as γ is beyond 1.2, the moment markedly decreases until it substantially vanishes with $\gamma > 1.4$. These results suggest that the T to MnBi phase transition could never occur in specimens having such a high γ-value. Using optical microscopy, however, we could verify that the T-phase formation has been completed in these specimens. Consequently it may be concluded that if the specimen with

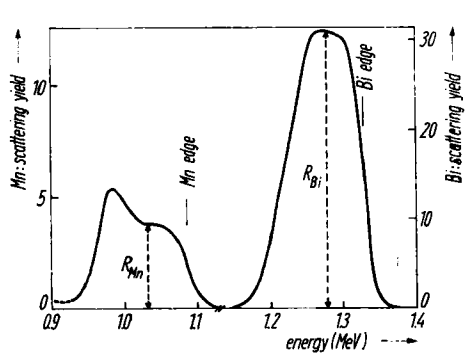


Fig. 8. Backscattering energy spectrum ($\times 10^3$) for the specimen with $\gamma = 1.4$, annealed at 250 °C for 4 h

$\gamma = 1.8$ is annealed at 250 °C for 4 h, the total amount of Bi may be consumed to form the T-phase and the excess Mn remains unreacted. In fact, the X-ray diffractometry for the specimen can adequately reveal the crystal structure of the T-phase, as shown in Fig. 3.

Besides, the concentration profile within the same specimen was investigated by the aid of the RBS experiment. The spectrum obtained is shown in Fig. 8. A hump on the left side of the Mn spectrum represents the remaining excess Mn situated on the substrate side. On the other hand, the step extending on the right side of the Mn spectrum can be attributed to Mn atoms included in the T-phase. The Bi spectrum, of course, has a shape of a simple plateau showing a uniform distribution of Bi within the T-phase. Therefore, the height ratio of the Mn step to the Bi plateau can be used to roughly estimate a chemical composition, i.e., the atom ratio of Mn to Bi in the T-phase, by making use of the equation derived by Mayer et al. [5]. Thus, the atom ratio was determined as Mn/Bi = 1.2, and the T-phase may be expressed by a chemical formula of $Mn_{1.2}Bi$.

Now, on the basis that the T-phase is assumed to be $Mn_{1.2}Bi$, let us consider how the whole reaction proceeds, if a double layer specimen with $\gamma > 1.2$ is annealed at 250 °C. In this case, the Bi atoms involved will be entirely consumed until the T-phase formation is completed. As a result, we have the T-phase together with some excess Mn, but no Bi is left behind. The experimental result shown in Fig. 7 has revealed that such a specimen would hardly be transformed even if the annealing is continued further. In the case where γ is less than 1.2, however, the circumstances are quite different. When the T-phase formation is completed, the Mn atoms will be entirely consumed, but some excess Bi will remain within the T-phase. Only in such a case, the final transformation into MnBi can take place on further annealing. We may reasonably conclude, therefore, that the remaining Bi does serve as a nucleus for the formation of MnBi crystals.

Table 1
Variation of intensities for Bi diffraction lines with annealing temperature

annealing	peak height	
temp. (°C)	(003)	(102)
as-evap.	110	520
220	160	150
250	500	50

Now, let us focus much attention uponr the emaining Bi, especially with respect to the crystal orientation. As noticed previously, the intensity ratio of Bi(003) line to Bi(102) line in the diffraction pattern can be taken as a measure to estimate the degree of a preferential orientation of Bi crystals. Accordingly, by referring to Fig. 2, the change in the intensity ratio accompanied with annealing is summarized in Table 1. Whereas the ratio is about 5 in the as-evaporated state, it becomes about unity at 200 °C and then it remarkably increases to 10 at 250 °C, where the T-phase formation has been completed. This fact implies that the remaining Bi crystals exhibit a distinct preferred orientation at this moment. It is probably because either the Bi crystals with random orientations are preferentially spent for the T-phase formation, or they recrystallize to achieve the preferred orientation during annealing up to 250 °C. In any case, if such a Bi crystal with its c-axis perpendicular to the film

plane may serve as a nucleus, we must obtain a well-orientated MnBi thin film, just like the present experiment has shown.

It has to be remarked, however, that in the final stage of reaction only a few excess Bi crystals serve as nuclei, and a substantial part of them remains still after the whole reaction is completed. The fact can be easily recognized with the X-ray diffraction pattern of Fig. 2d, where we can see that a considerable amount of Bi remains in the final stage of 250 °C, 4 h annealing. It seems to suggest that Bi acts as a nucleus to pull a trigger of the final reaction, i.e., the transition of T to MnBi, but Bi is little consumed in it. If this is the case, Bi as well as Mn initially evaporated may not react in a simple and stoichiometric manner in Williams' method.

By taking an example of the specimen with $\gamma = 1.1$, we shall consider again how the reaction proceeds. The reaction of the T-phase formation can be expressed by the following equation:

$$1.1\ \mathrm{Mn} + \mathrm{Bi} = 0.92\ \mathrm{Mn_{1.2}Bi} + 0.08\ \mathrm{Bi}\ . \tag{1}$$

This equation means that if 1.1 mole of Mn and 1 mole of Bi react, we obtain 0.92 mole of T-phase and the remaining 0.08 mole of Bi. Suppose that Bi is kept unreacted and the T-phase is independently transformed into the MnBi phase, we should obtain only 0.92 mole of MnBi. Consequently we have a rather imperfect MnBi thin film, because it includes a small amount of unreacted Bi as well as Mn. The saturation magnetization of the film thus prepared should be somewhat reduced in comparison with that of the perfect MnBi thin film. In fact, it has been found that the saturation magnetization is lower by about 10% than the nominal value, as previously described. Similar circumstances could be confirmed by using the specimen with $\gamma = 1.0$ also. In this case, the equation of the first step of reaction can be written as

$$\mathrm{Mn} + \mathrm{Bi} = 0.83\ \mathrm{Mn_{1.2}Bi} + 0.17\ \mathrm{Bi}\ . \tag{2}$$

Accordingly, even if equal numbers of Mn and Bi atoms are deposited as a starting material, only a fraction of 0.83 can react to form the final MnBi compound, and the rest of Bi and Mn atoms probably remain unreacted within the MnBi thin film. This situation should be emphasized to be quite different from that prepared by Chen's method. However, it is still unsolved where the remaining Bi and/or Mn atoms are situated.

4. Conclusion

The formation process of MnBi thin film prepared by Williams' method has been investigated by means of X-ray diffraction, TEM, RBS, and magnetic measurements. By summarizing the obtained results, we can illustrate the process as shown in Fig. 9, where the two cases with $\gamma > 1.2$ and $\gamma < 1.2$ are separately shown in the left and right rows, respectively.

As the film specimen is heated up to 250 °C, Mn atoms diffuse into the Bi layer to form a transitional compound phase which is composed of $\mathrm{Mn_{1.2}Bi}$ and is named T-phase. The T-phase does not exhibit ferromagnetism and consists of rod-like fine particles. In the former case, the whole reaction is finished when all Bi atoms are consumed to form the T-phase. As a result, we cannot attain the final ferromagnetic MnBi film. In the latter case, however, when the T-phase formation is completed, there remains still a small amount of excess Bi. As the annealing is continued further at 250 °C, a few remaining Bi crystals act as nuclei to proceed the further transition of the T-phase to the ferromagnetic MnBi. That is, the MnBi crystallizes there, growing at the expense of the T-phase over the whole specimen. Since the remaining Bi has a prominent texture in which its c-axis is perpendicular to the film, the final MnBi thin film can possess the preferred orientation of its c-axis inherited from the Bi

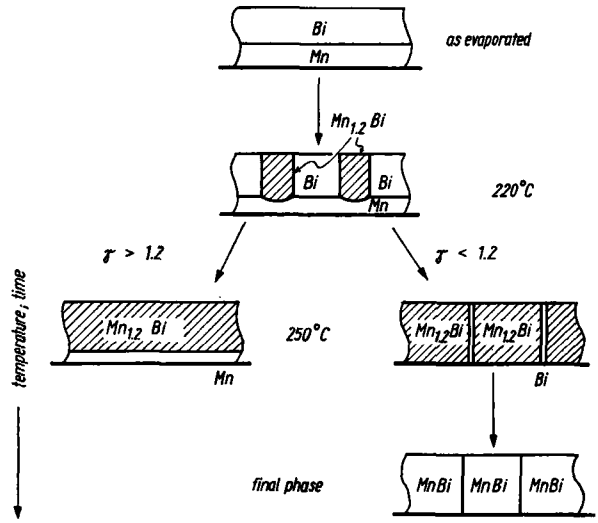


Fig. 9. Schematic illustration for the formation process of MnBi thin films prepared by Williams' method with different values of the deposition atom ratio

nuclei. It is to be noted, therefore, that as long as Williams' method is used, we cannot avoid a small quantity of unreacted Bi as well as Mn to be included in the final MnBi thin film.

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