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An Electron Microscopic Study on MnBi Thin Films

T. S. LIU
Honeywell Corporate Research Center, Hopkins, Minnesota 55343, USA

The structure and orientation of MnBi thin films prepared by sequential evaporation of bismuth and manganese on glass substrates were studied by transmission electron microscopy and electron diffraction. Results indicate that these films develop a preferred orientation with the *c*-axis perpendicular to the film plane. This preferred orientation is due to the formation of MnBi from a highly oriented bismuth layer, i.e., a layer with the *c*-axis perpendicular to the film plane. Trace amounts of elemental bismuth, manganese and MnO are found in these MnBi films. There is evidence of close parallel alignment between the MnBi and the bismuth lattices.

1. Introduction

Owing to its unusual magnetic and magneto-optic properties, MnBi has attracted the attention of research workers for a long time. Most of the early investigations were made on bulk MnBi. However, MnBi forms by a peritectic reaction [1] and it is difficult to attain equilibrium MnBi in bulk form. Instead, conditions conducive to solid state inter-diffusion between manganese and bismuth atoms must be used to promote MnBi formation. This requires large areas of contact between Mn and Bi. Thin films offer an excellent geometry for MnBi formation because their large surface-to-volume ratio facilitates solid-state diffusion. Williams *et al.* [2] first prepared MnBi thin films to demonstrate magnetic writing. Since then various investigators have demonstrated the potential applications of MnBi thin films in optical mass memories [3–6]. While the magnetic, optical, thermal and other physical properties have been documented, there have been few published reports on the structural aspects of MnBi thin films. Mayer [7] performed cursory nucleation experiments on MnBi thin films. Unger *et al.* [8] reported some structural aspects on MnBi/mica films in their study on growth of MnBi films on mica substrates. So far, no detailed structural study of MnBi thin films has been reported in the literature.

One convenient way to prepare MnBi thin films with controlled structure is by annealing layers of sequentially evaporated bismuth and manganese to effect a solid state reaction [9]. The structure of this type of MnBi thin film is the subject of this paper.

Optical microscopy provides one useful tool for the routine examination of MnBi thin films and the magnetic structure may be revealed by either the Faraday effect (transmitted polarised light) [2] or the Kerr effect (reflected polarised light) [10]. However, because of the small grain size and the extreme uniformity in MnBi films, optical microscopy is not suited for detailed structural examination. On the other hand, transmission electron microscopy does provide a powerful tool capable of revealing the structural details of these films. In addition, selected-area electron diffraction can provide information on the phases present, grain orientation and texture of the films. This paper describes results obtained during a transmission electron microscopic study of MnBi thin films.

2. Experimental Procedure

MnBi films were prepared by annealing sequentially evaporated layers of bismuth and manganese to effect a solid-state reaction. For these experiments, glass substrates were used. The structure and orientation of the resultant MnBi film is profoundly influenced by that of the original bismuth and manganese layers. It is, therefore, necessary to examine individual films of bismuth and manganese, and unannealed bismuth-plus-manganese, to gain a better understanding of the

resultant structure and orientation of the annealed MnBi films.

The elemental bismuth and manganese used for vapour sources were of 99.999 % spectroscopic grade. The bismuth and manganese were loaded in separate tungsten boats and evaporated by resistance-heating in a vacuum. Vacuum before deposition ranged from 5×10^{-7} to 2×10^{-6} torr. The normal evaporation rates were 180Å min^{-1} for bismuth and 300 to 400Å min^{-1} for manganese.

The reason that transmission electron microscopy has not been extensively utilised in studying MnBi thin films is that it is difficult, if not impossible, to separate the MnBi films from their substrates. To overcome this difficulty a special technique was developed which might be applicable to other vapour-deposited thin films which are hard to strip from their substrates. In this technique, the glass substrate was first partially covered with an evaporated amorphous carbon film. Bismuth plus manganese was then deposited on this substrate in the usual manner by evaporation and reacted to form MnBi. It was found that the portion of MnBi film with the intermediate carbon layer between it and the glass could be stripped off with a dried collodion overlayer. The collodion was subsequently dissolved, leaving a MnBi film suitable for study in the electron microscope. No carbon intermediate layer was needed for elemental bismuth because these films could be stripped readily from the glass substrate.

To ensure that the introduction of the carbon layer does not alter the structure and properties of the MnBi, MnBi/C/glass films were examined under polarised light using the Faraday effect. It was found that the magnetic domains were continuous and unchanged in size or shape in crossing from the region with the underlying carbon layer to the uncoated region. In addition, measurements of various magnetic properties, (e.g. coercive force, saturation magnetisation, total Faraday rotation, etc.) in these two regions also resulted in comparable values. On the basis of these observations it is believed that the structures of the MnBi specimens thus prepared are representative of MnBi films on glass substrates.

3. Results

3.1. Elemental Bi Films

Bismuth films can be prepared easily by vapour-deposition. When deposited at a rate of approximately 180Å min^{-1} in a vacuum of about 1×10^{-6} torr onto glass substrates at 60°C, the resultant Bi film showed an equiaxed grain structure with an average grain diameter of 1300Å (fig. 1). At approximately 100000 × magnification, dislocations suggestive of small-angle grain boundaries could be noticed between many grains upon proper tilting of the film specimen. This is shown at the arrows in fig. 1.

The grains of Bi also show bend contour fringes indicating buckling of the individual grains due to internal stress. These stresses probably arise from differential thermal contraction from the deposition temperature.

The crystallographic orientation and texture of the bismuth films can be accurately determined by X-ray and electron diffraction techniques. X-ray diffractometer tracings on Bi films show a single, strong peak corresponding to the normally weak basal plane (003) reflection. This indicates that the films are highly textured. This finding is substantiated by the electron diffraction results. A typical selected area electron diffraction pattern taken on the bi films is shown in fig. 2. The diffraction rings are all from (hk 0) type prismatic planes while the basal reflection is missing – indicating that the c-axes are indeed perpendicular to the film plane. The even intensity around the circumference of the diffraction rings indicates a random distribution of the a-axes in the film plane. The grainy nature of the lines is due to the relatively large grain size in these bismuth films. Evaporated bismuth films exhibit the same crystal structure and lattice parameters as the bulk form.

In summary, then, bismuth films deposited on glass show a highly textured structure with the c-axis located perpendicular to the plane of the film and with random orientations about that axis.

3.2. Elemental Mn Film

Evaporated manganese films cannot be stripped from glass, consequently only films deposited with a carbon intermediate layer have been studied. When deposited at a rate of approximately 300 to 400Å min^{-1} in a vacuum of 2×10^{-6} torr onto a supported carbon substrate at 60°C, the resultant Mn films show an equiaxed grain size of the order of 260Å (fig. 3).

Owing to this relatively fine grain size and generally random orientation, the electron diffraction pattern consists of diffuse rings with uniform intensity around their circumference

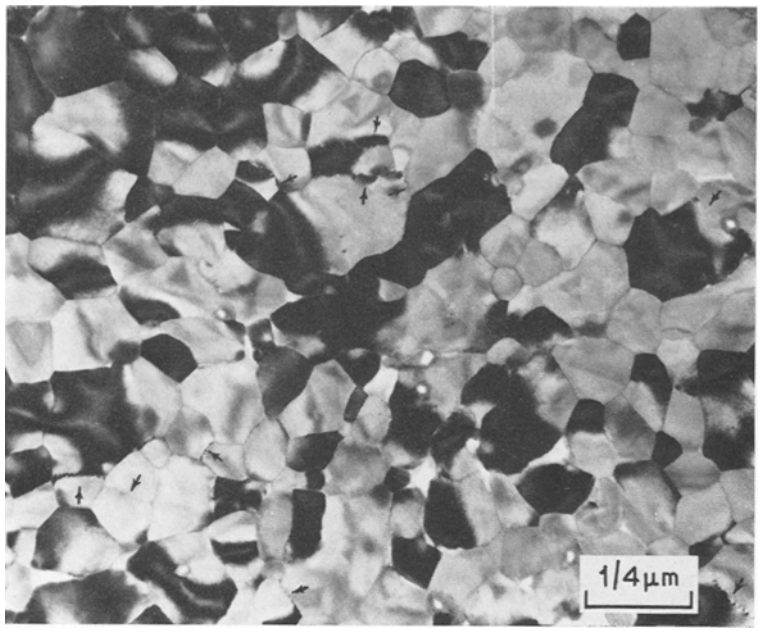

Figure 1 Bismuth thin film deposited on glass substrate at 60° C.

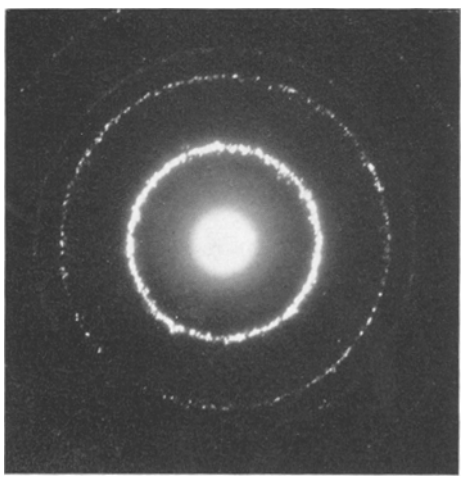

Figure 2 Electron diffraction pattern of an area in fig. 1.

(fig. 4). Unlike bismuth thin films, no strong diffraction peak is observed on X-ray diffractometer tracings. These results indicate that when elemental manganese is deposited onto a glass substrate in this manner, the resultant film does not exhibit any preferred orientation.

In bulk manganese, the stable form at room temperature is the alpha phase which is simple cubic in structure with $a_0 = 8.913$Å [11]. While the stronger diffraction lines in the electron diffraction pattern (fig. 4) of this film are due to Mn diffraction, most of the weaker lines can best be indexed on the basis of MnO, which is of sodium chloride structure with $a_0 = 4.445$Å [12]. Considering the affinity of manganese to oxygen and the vacuum employed in manganese vapour deposition, some degree of oxidation is not unexpected.

3.3. Unannealed Bismuth Plus Manganese

When manganese (250 to 300Å thick) was deposited on top of a bismuth film (500 to 600Å thick) on a glass substrate, the resulting Mn + Bi film structure was dominated by that of the bismuth film. This was probably due to the combined effect of the larger grain size of the bismuth film and the thinness and the near-amorphous nature of the manganese overlayer. Fig. 5 shows a typical unannealed Mn + Bi film stripped from a carbon/glass substrate. The grain boundaries were not as sharply defined as was found in the elemental Bi films. In addition, areas within the grains were hazy and could not be resolved even at 100000 ×. This was presum-

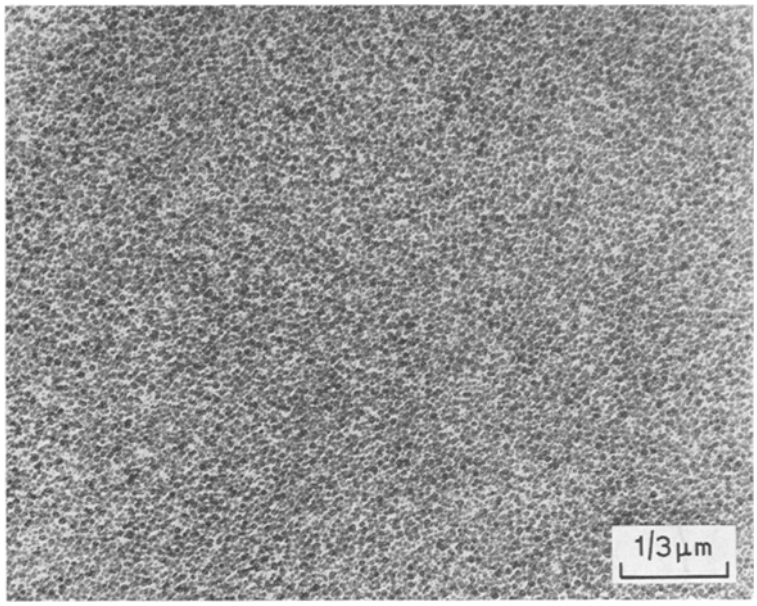

Figure 3 Manganese thin films deposited onto carbon/glass at 60°C.

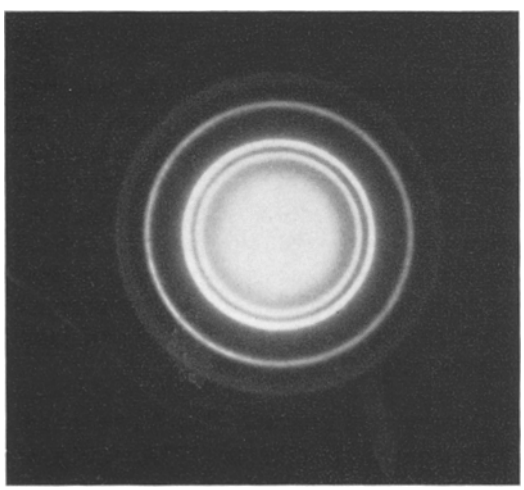

Figure 4 Electron diffraction pattern of an area in fig. 3.

ably due to the presence of the near-amorphous manganese and MnO overlayer.

The electron diffraction pattern taken on this film was composed of two distinct sets of diffraction lines as expected (fig. 6). The set of grainy lines was, as before, due to bismuth, and the set of diffused, smooth lines due to manganese and MnO. It was noticed that the bismuth diffraction rings did not have an even intensity around their circumference as was the case of bismuth films without the overlayer. Distinct arcs were apparent, suggesting a preferred orientation of *a*-axes within the basal plane. This is a further preferred orientation in the bismuth film which has already aligned its *c*-axes perpendicular to the film plane.

3.4. Annealed MnBi Films

After reacting Mn and Bi (with the manganese deposited on top of the bismuth) to form MnBi at 300°C for 6 h, the resultant MnBi film consisted of a complex mixture of large and small equiaxed grains (fig. 7). The grain sizes ranged from below 1000Å to about 3000Å. The sharpness of the bend contour fringes indicate buckling slightly more severe than in the original Bi films. These contours generally terminate at grain boundaries. The electron micrograph does not exhibit a typical single-phased structure. One additional interesting aspect of these micrographs is the presence of moiré fringes in the vicinity of the bend-contour extensions. They become resolvable at about 100000 ×. This is indicated by arrows in fig. 7.

A typical selected area electron diffraction pattern taken on MnBi films is shown in fig. 8. This pattern shows three distinct sets of diffraction lines: 1. Smooth continuous rings, 2. Spotty rings and 3. Multiple spotty rings – doublets

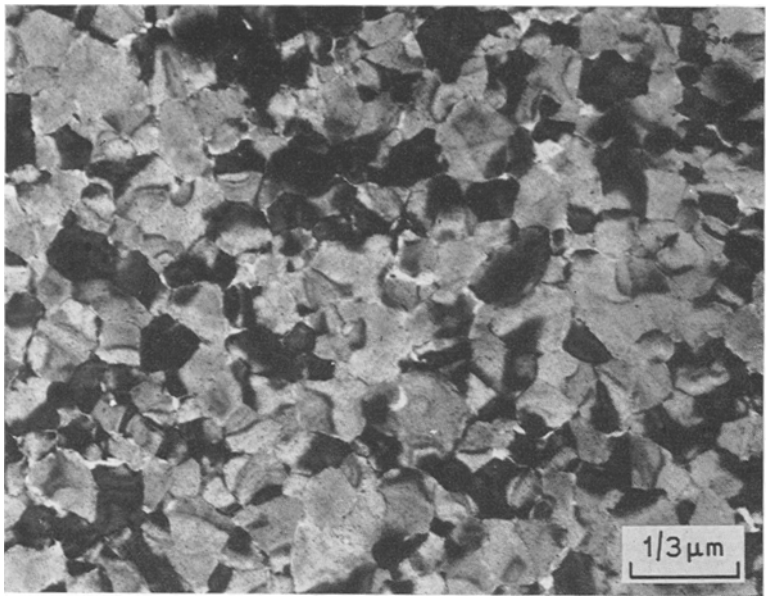

Figure 5 Thin film of bismuth with manganese overlayer, carbon/glass substrate at 60°C.

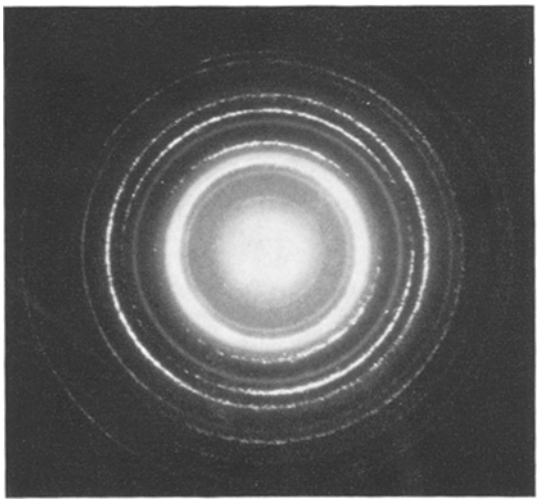

Figure 6 Electron diffraction pattern of an area in fig. 5.

and triplets.

On the basis of the observation on electron diffraction patterns on Bi, Mn and unannealed Bi films with Mn overlayers discussed above, one recognises that the smooth and spotty rings are in all likelihood due to residual Mn + MnO and Bi present, respectively. The multiple rings can be interpreted by considering the lattice relationship between bismuth and MnBi.

X-ray diffractometer profiles taken on MnBi films thus prepared showed a single high intensity peak corresponding to the usually weak (00 2) MnBi basal plane reflection [13]. This result, in addition to our knowledge of the orientation of bismuth films and the moiré fringes observed above, points to the fact that, similar to bismuth film, the MnBi film is also orientated with its *c*-axis perpendicular to the film plane.

Table I lists the interplanar spacings, Miller indices of the diffracting planes and the observed intensities and other characteristics of the diffraction lines in fig. 8. A detailed discussion on the interpretation of this diffraction pattern is given in the next section.

From the evidence obtained on examining transmission electron micrographs of films of MnBi and their electron diffraction patterns, one has to conclude that there is residual elemental bismuth, manganese and MnO in addition to the MnBi in these "MnBi" films. Similar results are obtained on specimens annealed for 16 h at 300°C.

4. Discussions

4.1. Unannealed Films

It is interesting to note that while in a randomly oriented bismuth sample (10 2) planes produce the strongest diffraction, in bismuth films the strongest electron diffractions are from (1 1 0) planes. The reason for this is that in a hexagonal

TABLE I

Line No.	d_{calc} (Å)	*hkl*	*d* Reported* from X-ray	Material	I_{Obs}	Remarks
1	3.70	100	3.690	MnBi	vw	Spotty
2	3.28	102	3.28	Bi	vw	Spotty
3	2.57	111	2.568	MnO	m	Smooth
4	2.24	110	2.273	Bi	vs	Spotty doublet
5	2.14	110	2.137	MnBi	vs	
6	2.10	†	2.09	Mn	m	Broad, smooth
7	1.57	220	1.571	MnO	m	Smooth
8	1.31	300	1.312	Bi	s	Spotty doublet
9	1.24	300	1.237	MnBi	s	
10	1.21	†	1.21	Mn	vw	Smooth
11	1.12	220	1.1368	Bi	w	Spotty triplet
12	1.08	220		MnBi	w	
13	1.06				w	

*Roberts [14]; Swanson *et al.* [12, 15].
†No Miller indices were given on the simple cubic α-Mn. These are the two strongest lines according to the ASTM card file.

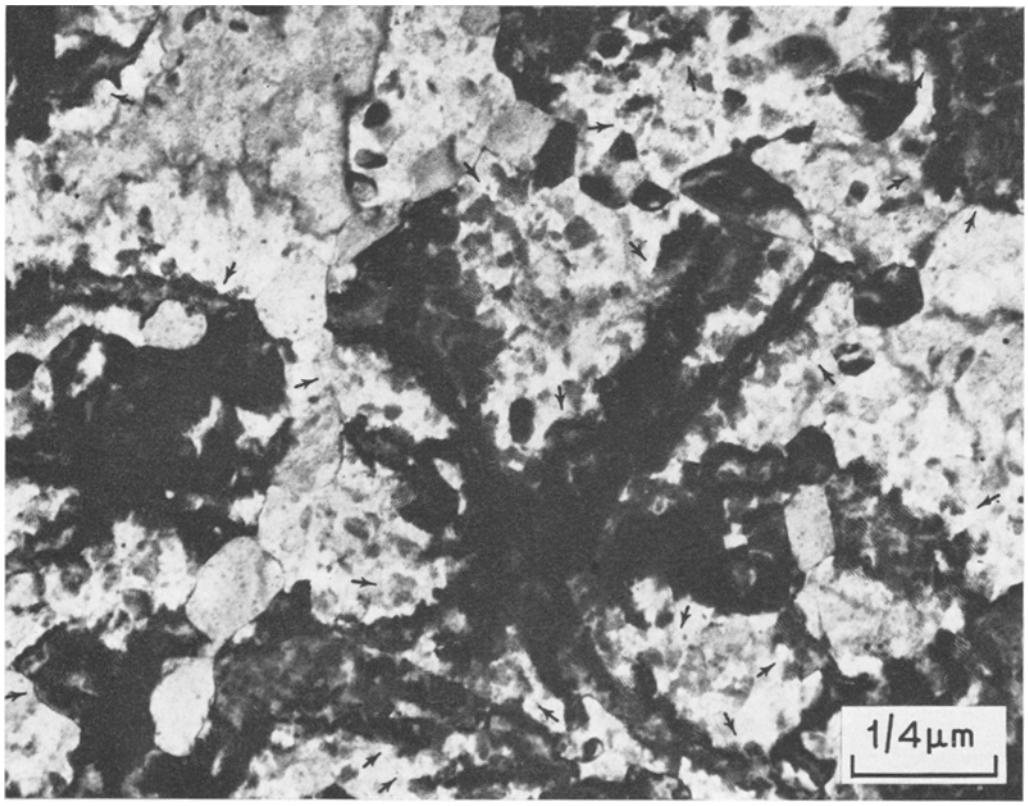

Figure 7 Thin film of MnBi prepared on carbon/glass substrate.

film with the *c*-axis oriented perpendicular to the film plane, (102) is a "forbidden" plane in normal transmission electron diffraction conditions and of the planes which satisfy the (*hk*0) condition, (110) planes produce the strongest diffracted intensity.

However, in all the diffraction patterns of bismuth films examined, there is, in addition, a very faint, smooth ring, or at times a few faint spots present which cannot be indexed as a (*hk*0) diffraction, but fits very well on the basis of the (102) diffraction. This diffraction line is

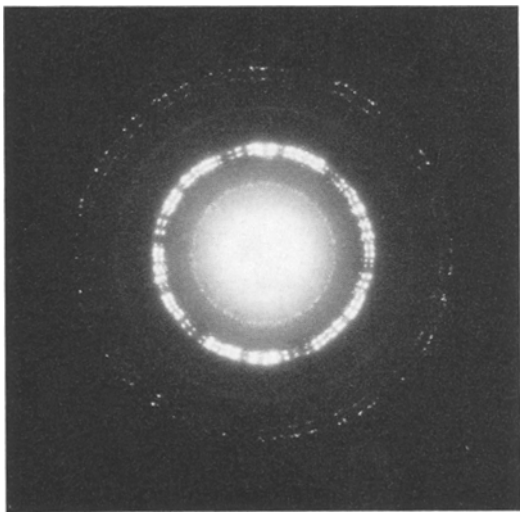

Figure 8 Electron diffraction pattern of an area in fig. 7.

also observed in annealed "MnBi" films (see table I above). Since this is a "forbidden" diffraction in a perfectly oriented film with *c*-axis perpendicular to the film plane, one is forced to the conclusion that while nearly all the bismuth in these films are oriented with its *c*-axis perpendicular to the film plane, there is nevertheless a minute amount of randomly oriented bismuth present.

In the electron diffraction pattern shown on unannealed Bi thin film with Mn overlayer (fig. 6) one notices that it is dominated by bismuth diffractions. Although manganese was deposited on top of bismuth, only the strongest manganese diffractions appear. This is believed to be due to the combined effect of the approximately 2:1 Bi to Mn volume ratio in the MnBi film used and the much higher atomic scattering power of bismuth. The distinct characteristics of the elemental Bi, Mn and MnO diffractions is retained in this diffraction pattern. Aside from the development of further preferred orientation of the a_0 axes of Bi in the film plane mentioned previously, this film consists essentially of a mixture of bismuth, manganese and MnO.

4.2. Annealed MnBi Films

The moiré fringes observed in fig. 7 are considered as convincing evidence that the MnBi forms epitaxially on orientated bismuth. Since manganese atoms are considerably smaller than atoms of bismuth, it is conceivable that they are more mobile during MnBi formation. Moiré fringes originate from either a small difference in crystallographic plane spacing or a small difference in orientation between the various phases present, or more likely, a combination of the difference in plane spacing and crystallographic orientation. Owing to the similarity of crystal structure between bismuth (rhombohedral, which can be considered hexagonal) and MnBi (nickel arsenide type, also hexagonal) the moiré patterns in this instance is in all probability due to the epitaxy of MnBi on the oriented Bi crystals.

The moiré fringes observed could arise from one of the $\{hk0\}$ reflections – either the $\{110\}$ or the $\{300\}$ reflections of Bi and MnBi. Using the electron diffraction *d*-values given in table I, moiré spacings of 48Å and 23Å are calculated for $\{110\}$ and $\{300\}$ reflections respectively [16]. Measurement of moiré spacings in fig. 7 gives a value close to 50Å. It seems therefore likely that the moiré fringes observed arise from the $\{110\}$ reflections.

The electron micrographs and diffraction patterns of these "MnBi" films, although complex, are quite reproducible. Results reported here are based on the examination of some fifty electron diffraction patterns calibrated by superimposing with evaporated gold film. The doublets and triplets observed (fig. 8) are characteristic of these films. The doublets are due to the $\{110\}$ and $\{300\}$ reflections of the bismuth and MnBi. This arises because the two lattices are in parallel. This condition is conducive to multiple diffraction which may account for the triplets observed.

5. Conclusions

In summary, this work has shown that MnBi thin films obtained on glass substrates by the sequential evaporation of Bi and Mn followed by reaction at 300°C for 6 h exhibit the following characteristics:

(1) Equiaxed grains with grain size ranging from under 1000Å to about 3000Å.

(2) Preferred orientation with *c*-axes perpendicular to the film plane. The *a*-axes orientation within the film plane is random.

(3) The film contains residual Bi, Mn and MnO in addition to MnBi.

(4) Moiré fringes indicating epitaxial growth of MnBi on the original Bi layer.

(5) Multiple electron diffractions indicate a closely parallel alignment of the MnBi and bismuth lattices.

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