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Magnetic properties of low temperature phase MnBi of island structure

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The magnetic and structural properties of island-structured LTP MnBi fabricated onto MgO single crystal substrates are discussed. The size and height of the “Volmer-Weber” type islands vary from place to place but are averagely a few microns and sub-microns, respectively. From the wetting angle (40~60°) of those islands, the surface energy γ_{MnBi} of LTP MnBi is found to be 0.5~0.8 J/m². Those MnBi islands possess the magnetic anisotropy constant K_u and saturation magnetization M_s close to those for bulk over a temperature range of 5 to 400 K. There seems to be a correlation between K_u and lattice constant c measured at 300K. The K_u is found to be inversely proportional to M_s^5 over the temperature range from 5 K to 400 K, as compared to the M_s^8 dependence for those fabricated onto fused silica glass substrates. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4943148>]

I. INTRODUCTION

Among various high magnetic anisotropy materials such as SmCo₅ and Fe₁₄Nd₂B, the low temperature phase (LTP) MnBi exhibits a significant increase of the uniaxial magnetic anisotropy constant K_u with temperature T over a temperature range from about 100K to about 500K, in the order of 10⁷ erg/cc for T beyond about 250K.¹⁻⁶ Therefore, the LTP MnBi is attractive for permanent magnet applications operated at elevated temperatures. Much work has been reported in literature to elucidate both experimentally and theoretically this unique temperature dependence of K_u .²⁻⁶ A recent experimental work of the temperature dependence of K_u in the LTP MnBi thin films deposited onto silica glass substrates showed that K_u was *inversely* proportional to the 8th power of the saturation magnetization M_s . Such a strong (inversely) dependent K_u on M_s has not been reported in any other materials up till now. It was also found that the K_u was proportional to the unit cell volume.⁶ The theory based on first principles calculation of magnetic anisotropy energy as function of lattice constants (a and c) was found to be qualitatively in agreement with the experimental results, but the transition at around $T = 100\text{K}$ from the in-plane to the out-of plane direction for the easy axis for magnetization is not accounted for.^{4,6} Despite the voluminous works reported, the detailed mechanism for the origin of the magnetic anisotropy is still open to question. Since the magnetic anisotropy is significantly dependent on lattice constants a and c , the present study has been motivated to study the effect of the lattice constant on magnetic anisotropy for the LTP MnBi films by choosing single crystal substrates of MgO with various orientations.

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II. EXPERIMENTAL

Multilayers of $[\text{Mn} (x \text{ nm}) / \text{Bi} (y \text{ nm})] \times N$ ($x=2, y=1\sim 8, N=1\sim 10$) were deposited onto MgO (100), (110) and (111) single crystal substrates at an ambient temperature by using a DC magnetron sputtering system. The deposition rates for Bi and Mn were 0.07 nm/s and 0.02 nm/s, respectively. Then, the samples thus fabricated were annealed in vacuum better than 10^{-8} Torr at various temperatures T_a for times t_a . A 5nm thick Ru capping layer was deposited after the annealing.

Measurements of the temperature dependence of magnetic properties were carried out by using a vibrating sample magnetometer in fields up to 9T over a temperature range from 4K to about 400K. The uniaxial magnetic anisotropy constant K_u was estimated by torque magnetometer for the out-of-plane mode in fields up to 9T over the temperature range mentioned above. The K_u values were obtained by extrapolating the amplitude of the two and four fold symmetry components to an infinite field strength, defining K_u as $(K_{u1} + K_{u2})$, where K_{u1} and K_{u2} are the first and second magnetic anisotropy constant in the hexagonal formula, respectively.

The crystal structure of the films thus fabricated was characterized by X-ray diffraction (XRD) with Cu ($K\alpha$) and Co ($K\alpha$) radiation, by transmission electron microscopy (TEM), and by scanning electron microscopy (SEM), together with energy-dispersive X-ray spectroscopy (EDX).

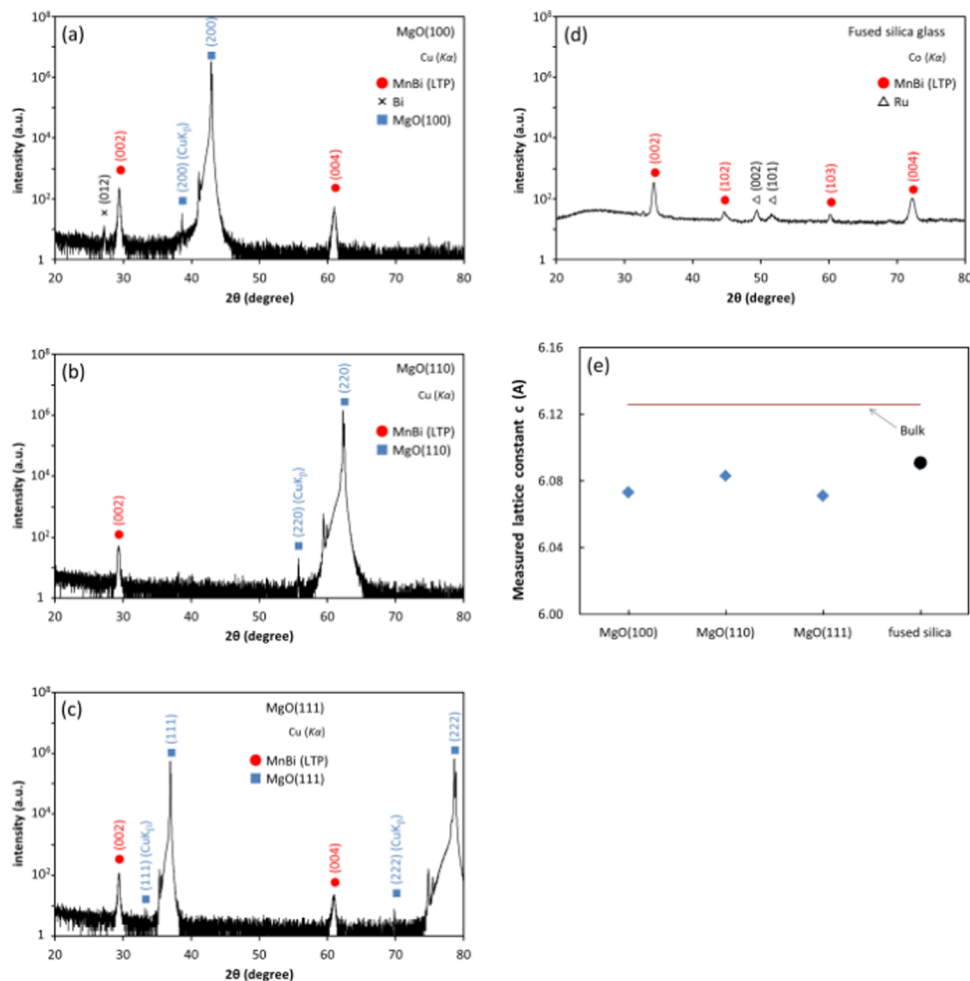


FIG. 1. (a-d). The XRD patterns for the films fabricated onto MgO (100), MgO (110), and MgO (111) substrates, together with that onto the fused silica glass. (e) The lattice constant c at 300K for the samples fabricated onto the various substrates as designated in the figure, together with the values for bulk.⁸

III. RESULTS AND DISCUSSIONS

Figure 1(a), 1(b) and 1(c) show the XRD patterns for the $\{\text{Mn}(2\text{nm})/\text{Bi}(3.2\text{nm})\times 10\}$ films fabricated (T_a and t_a were 450°C and 0.5hr , respectively) onto MgO (100), (110) and (111) substrates, respectively, together with the result for the silica glass substrates for which T_a and t_a were 550°C and 0.5hr , respectively.⁷ It is clearly seen that all the samples are of the low temperature phase with the c -axis orientation along the film normal. The lattice constant c for those films is shown in Fig. 1(e). The values of c are 6.073, 6.083, 6.071 and 6.09 Å for MgO (100), (110), (111) and fused silica substrate, respectively, which are all smaller than the bulk value ($=6.125\text{Å}$) by about 1%.⁸

Figure 2(a) shows the SEM image of the sample-surface of the sample fabricated onto the MgO (100) substrate. The image clearly shows the island structure of the LTP MnBi. Such island structure is also found for other cases of MgO (110) and (111). It is further noted that when the annealing condition changed to T_a and t_a were 450°C and 0.5hr for silica glass substrates, a similar island structure was also formed. The size of those islands varies from place to place, but averagely ranges from a sub-micron to several microns. Fig. 2(b) reveals that the islands are of a mountain-like shape with a height of approximately $1\mu\text{m}$, much larger than the nominal thickness for the present multilayer, which is 52nm . Fig. 2(c) shows the EDX results for atomic mappings of Mn, Bi, Mg

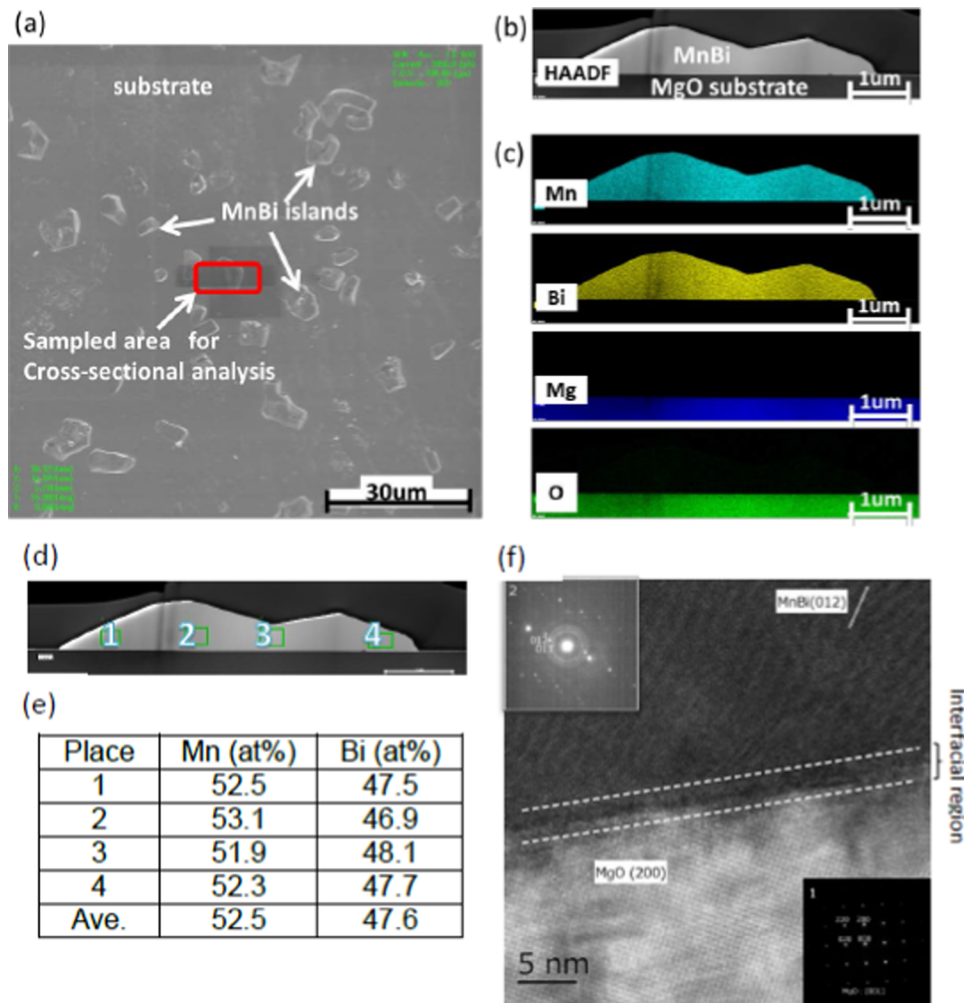


FIG. 2. (a) The SEM image for the LTP MnBi fabricated onto MgO (100) substrate ($T_a=450^\circ\text{C}$ and $t_a=0.5\text{hr}$). (b) The cross sectional TEM image. (c) The EDX image for each element for the MnBi island. (d,e) The compositional analysis of the MnBi island. (f) The high resolution TEM image for the island formed onto MgO (100) substrate, together with the diffraction patterns of MnBi and MgO(100) substrate.

and O. It is shown that the island has the uniform distribution of Mn and Bi elements, forming the LTP. The atomic contents of Mn and Bi at different positions within the island vary from position to position, but averagely 52.5 and 47.6 at%, respectively, as shown in Fig. 2(d) and 2(e). The result indicates that the LTP phase of MnBi island is of Mn rich phase. It is noted that this morphology is much different from the case for the LTP films deposited onto fused glass substrates at $T_a = 550^\circ\text{C}$ for 0.5 hr, where such island structure was not formed, but instead the film structure consisting of both the regions of LTP MnBi and Bi was formed.⁶

Figure 2(f) shows the high resolution cross-sectional image and the diffraction patterns from the MgO substrate and the MnBi island, as indicated by 1 and 2, respectively. The high resolution image of MgO shows a (100) lattice image. However, no clear lattice image is found in the MnBi film, but only a moiré fringe pattern. The diffraction pattern of 1 corresponds to the MgO (100)

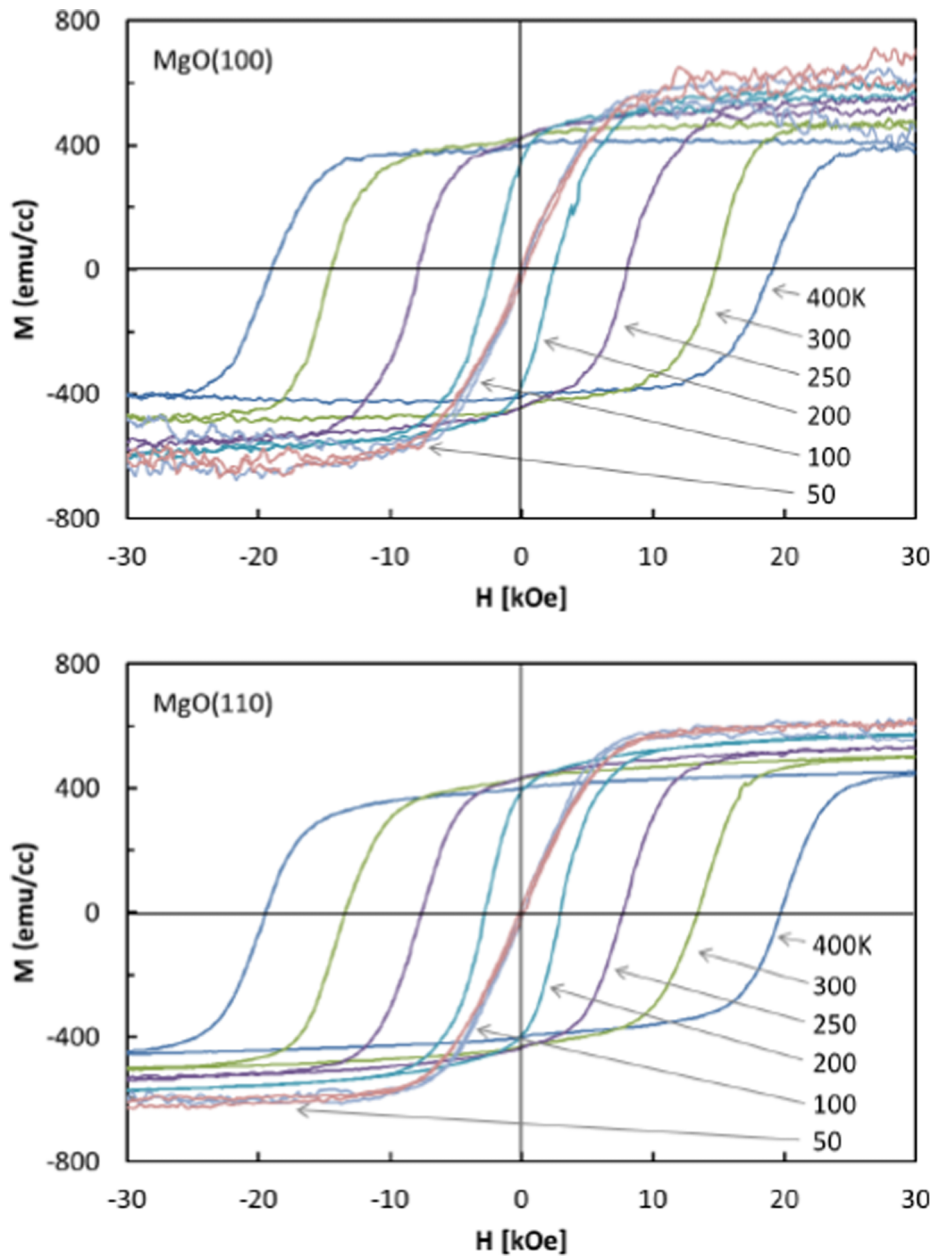


FIG. 3. The out-of-plane M-H curves for the MnBi islands at the various measurement temperatures, which were fabricated onto MgO (100) and (110) substrates. All the M-H curves exhibit the high remanence values except for $T=50\text{K}$.

plane, but the diffraction pattern of MnBi island shows very little evidence for the coherence in orientation. The same phenomenon was observed for the cases of MgO (110) and (111). It is also noted that there is a few nm thick interfacial region between the substrate and MnBi. While the XRD patterns for all the samples exhibit the *c*-axis orientation along the film normal, those TEM results are at variance with the XRD result. However, this discrepancy between the TEM and XRD analyses is not unusual if there be a dispersion in the *c*-axis orientation. To clarify the reason for this discrepancy, a more detailed analysis of the *c*-axis dispersion is in progress.

Such an island growth is known as Volmer-Weber growth-model, where a 3D islands formation takes place through a stronger binding of film-atoms to each other than to substrate and/or slow diffusion.⁹ In this case, one would not expect any close correlation in crystallographic orientation between the film and the substrate. High resolution images for all the cases of the MgO orientations shows little evidence to support an epitaxial growth in all the cases.

Surface energy is an important quantity in considering the evolution of microstructure in small-scale material system. One may estimate the surface energy γ_{MnBi} of the LTP MnBi island by using Young's equation for the wetting angle which is about 40~60 degree in the present case. By using the surface energy γ_{MgO} of MgO(100) to be 1.2 J/m² and that for the interface surface energy $\gamma_{\text{MnBi/MgO}}$ between MnBi and MgO(100) to be 0.8 J/m², one obtains γ_{MnBi} to be 0.5~0.8 J/m², where the surface energy γ_{Bi} of Bi is assumed to be 0.4 J/m².¹⁰ Therefore, a so-called spreading parameter *S*, which is defined as ($\gamma_{\text{MgO}} - \gamma_{\text{MnBi}} - \gamma_{\text{MnBi/MgO}}$), is negative (-0.1~-0.4 J/m²), meaning the island structure is preferable for MnBi onto MgO substrates.

Figure 3(a) and 3(b) shows the out-of plane M-H curves at different temperatures from 50 to 400K for the MgO (100) and (110) cases, respectively. All the curves shows a high squareness, except for that measured at 50K for both MgO (100) and (110). Fig. 4 shows the temperature dependence of coercivity H_c for both MgO (100) and (110), together with the data for fused silica glass substrate.⁶ It is of interest to note that all the films exhibit a very similar dependence of H_c on *T*, drastically increasing for *T* beyond 150 K and reaching to about 18 kOe at 350 K.

Figure 5(a) shows the saturation magnetization M_s as a function of temperature for MgO (100) and (110) cases, together with the results for bulk² and fused silica substrate.⁷ Here, the M_s values were estimate by interpolating *M*(*H*) over the range of *H* = 30~60 kOe to *H*=0 so as to exclude the paramagnetic contribution the magnetization if any. The M_s values at all temperatures thus obtained

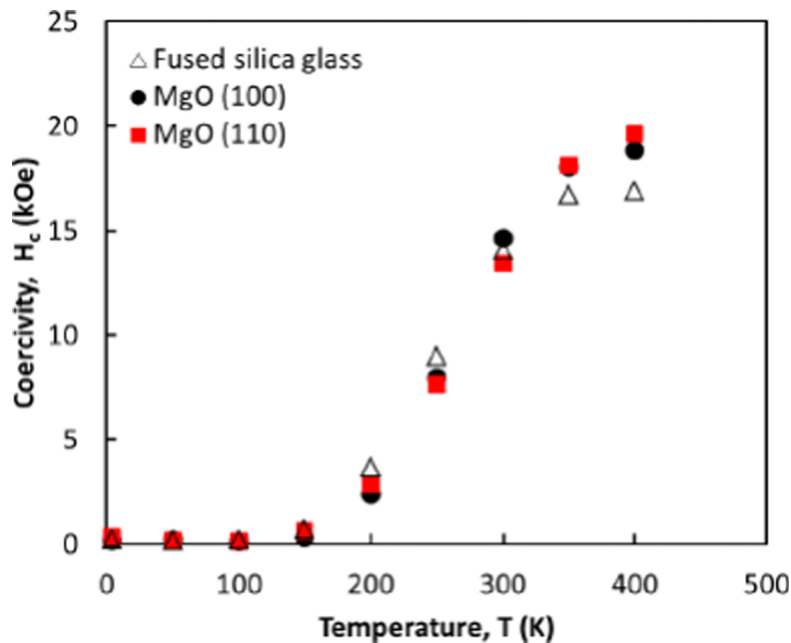


FIG. 4. The temperature dependence of coercivity H_c for the MnBi islands fabricated onto MgO (100), (110) and fused silica glass substrates.

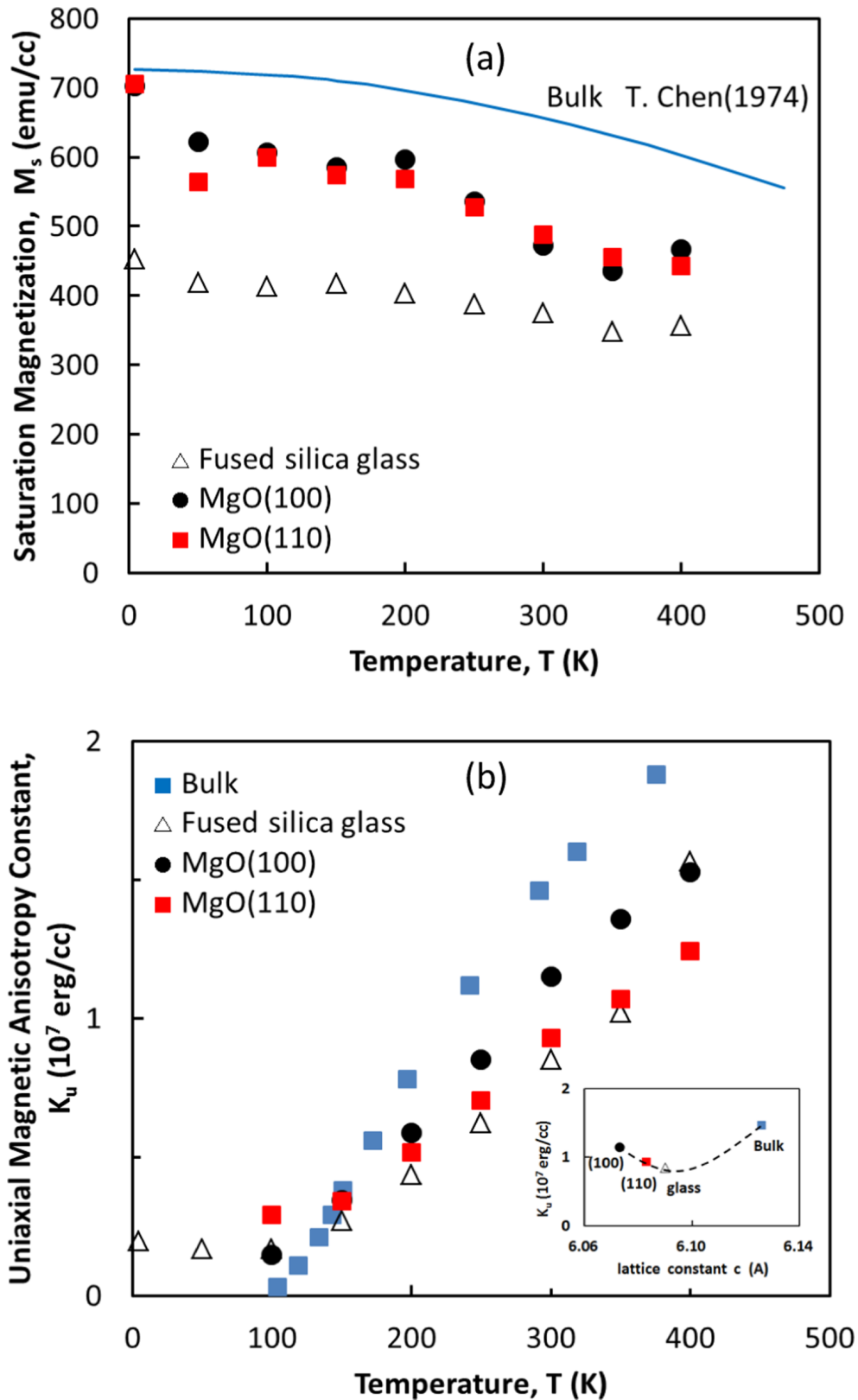


FIG. 5. The temperature dependence of (a) the saturation magnetization M_s and (b) the magnetic anisotropy constant K_u for the MnBi islands fabricated onto Mg (100), (110) and silica glass substrates, together with the bulk data.² Also shown in the inserted figure is the correlation between K_u and lattice constant c measured at 300K.

for both the MgO (100) and (110) cases are nearly the same, which are higher than that for the fused silica case by about 30%, but smaller than that for bulk by about 20%. The reason for this smaller M_s values than the bulk values are presumably due to the presence of other phases than the LTP, such as Bi, as revealed in the XRD pattern given in Fig. 1(a).

Figure 5(b) shows the temperature dependence of magnetic anisotropy constant K_u for both the cases of MgO (100) and (110), together with the data for the bulk and the fused silica substrates. The K_u values increase almost linearly with T beyond 150 K, reaching to about $K_u = 1.5 \times 10^7$ erg/cc at about 400 K for the MgO (100) case. It is pointed out that there remains the *positive* K_u values of order of 10^6 erg/cc for T even below 100K for the case of fused silica glass substrate, for which temperatures, the easy axis for magnetization for bulk is in the c -plane.²

In the inserted figure in Fig. 5, the correlation between K_u and lattice constant c at 300K is plotted. As mentioned above, the c values for all the present thin films are smaller by about 1% than that bulk value. It seems there is a trend for K_u with lattice constant c , but a further detailed study must be made for better understanding.

As discussed by theories, the magnetic anisotropy constant is more sensitive to lattice constant a than c .^{4,6} Since the lattice constant a is not known for those films deposited onto MgO substrates in the present study because of the c -axis orientation along the film normal, one cannot discuss the validity of the theoretical prediction. However, as far as its dependence on lattice constant c goes, the present result seems to suggest the correlation between K_u and c , as shown in Fig. 5.

The magnetic anisotropy mechanism has been discussed in terms of the correlation between magnetic anisotropy and saturation magnetization over a wide temperature range.¹¹⁻¹³ This information is useful to identify either single ion-model or two ions model predominant, as demonstrated elsewhere.^{6,13,14} Figure 6 shows the correlation between K_u and M_s for the cases of MgO (100) and (110), together with the result for the fused silica substrate⁶ and for bulk.² It is interesting to note that the correlation is nearly the same for both MgO (100) and (110), inversely proportional to M_s^5 . On the other hand, the correlation for the fused silica and bulk cases is inversely proportional to M_s^8 , and M_s^{11} , respectively.^{2,6} No theoretical prediction on LTP MnBi has been put forward to account for this correlation as yet.

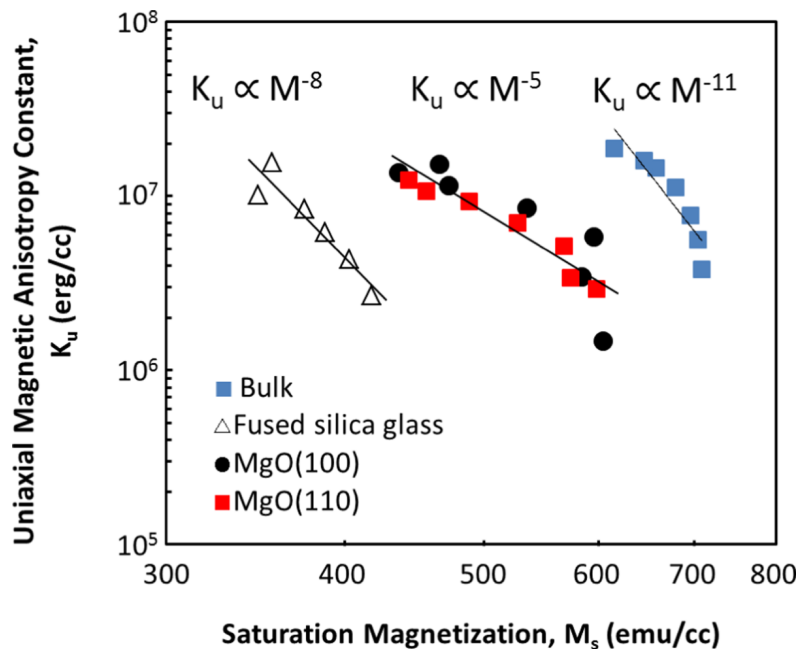


FIG. 6. The correlation between the magnetic anisotropy constant K_u and the saturation magnetization M_s for Mg(100), and (110), together with the data for the fused silica glass⁶ and bulk.² Note that the temperature ranges for MgO, fused silica and bulk are about 100 ~400K, 150~400K and 150~370K, respectively.

IV. SUMMARY

The island-structured LTP MnBi was, for the first time to the authors' knowledge, found to form onto MgO single crystal substrates. From the wetting angle of those island, the surface energy of LTP MnBi is estimated to be 0.5~0.8 J/m².

The MnBi islands possesses the easy axis for magnetization perpendicular to the substrate plane with the magnetic anisotropy constant K_u and saturation magnetization M_s close to those for bulk. There seems to be a correlation between K_u and lattice constant, c , measured at 300K. The K_u is found to be *inversely* proportional to M_s ⁵ over the temperature range from 5 K to 400 K, as compared to M_s ⁸ dependence for those fabricated onto fused silica glass.

ACKNOWLEDGEMENTS

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