Ferromagnetism above room temperature in Mn–Si–C alloy films

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Mn–Si–C alloy films are prepared by e-beam coevaporation onto a Si substrate held at 600 °C. Ferromagnetism is observed below $T_c=(360\pm5)$ K with SQUID magnetometry and magneto-optical Kerr effect. This is the highest Curie temperature T_c yet observed for a Mn-based alloy. Although the composition determined by Auger depth profiling varies appreciably for different films, their T_c is the same indicating that ferromagnetism is caused by an alloy of well-defined composition independent of precipitations. [S0003-6951(96)03122-1]

Recently, ferromagnetism in Mn/C/Si triple layers prepared by sequential deposition at 300 K was reported to occur above room temperature.[1] The onset of ferromagnetism was observed near 390 K and the saturation magnetization was depressed upon annealing above room temperature and vanished after annealing at ~520 °C. This suggests that some intermediate complex phase (or phase mixture) is formed at the interface(s) since neither Mn/Si or Mn/C bilayers support ferromagnetism.[1] Indeed, it is known that the intermetallic compound Mn_5Ge_3 is ferromagnetic below 304 K.[2,3] In alloys of $Mn_5(Si_xGe_{1-x})_3$ the Curie temperature decreases with increasing x.[4] It is therefore of interest to investigate Mn–Si–C alloys in search for ferromagnetism at elevated temperatures. In this letter we report on the direct formation of a Mn–Si–C alloy prepared by evaporation which is ferromagnetic at room temperature, with a Curie temperature $T_c\approx$ 360 K.

The samples were prepared by coevaporation of a SiC ceramic together with Mn (purity 99.98%) from two e-beam crucibles in an UHV chamber (background pressure $<10^{-10}$ mbar). The Si(001) substrate temperature was held at T_s = 450, 600, or 750 °C for different runs. Figure 1 shows x-ray diffractograms (Cu $K\alpha$ radiation) obtained in the $\theta/2\theta$ configuration for 2000-Å thick films prepared at different T_S. For T_s=450 °C only a broad maximum centered at $2\theta=43°$ was observed, possibly indicating the formation of an amorphous alloy at this rather low substrate temperature. For T_s=600 °C a few Bragg reflections occur between 43° and 47° which can be attributed to a majority phase with Mn_5Ge_3-type structure (hexagonal unit cell, space group $P6_3/mcm$[5]). The indicated line positions were obtained by a least-squares fit, yielding lattice constants of a = 6.95 Å and c = 4.82 Å, although with a large error due to the large width of the reflections. These values correspond to a lattice contraction of 3% and 4.5% for a and c, respectively, when compared to Mn_5Ge_3. In addition, a few peaks appear which indicate precipitation of elemental Si and Mn. Finally, for T_s=750° C most reflections can be identified as arising from the intermetallic compound $Mn_{27}Si_{47}$.

All samples were investigated with the transverse magneto-optical Kerr effect (MOKE). Experimental details are given elsewhere.[6] No ferromagnetic signal was detected down to 10 K for films prepared at T_s=750 °C, while for T_s=450 °C the onset of ferromagnetism was observed at 290 K. However, the MOKE signal was smaller by a factor of 20 compared to films with T_s=600 °C indicating only a very minor ferromagnetic fraction. Figure 2 shows an *in situ* Auger depth profile of a 2000-Å film prepared at T_s=600 °C across the whole sample, which yields an average composition $Mn_{21}Si_{34}C_{35}$. Another 2000-Å sample showed the average composition $Mn_{46}Si_{25}C_{29}$. The composition was simply evaluated by using elemental sensitivity factors,[7] without taking into account corrections due to matrix effects. In view of the predominance of the Si precipitation, a structure $Mn_5(Si_xC_{1-x})_3$ is therefore possible. Definite conclusions can, however, only be drawn after preparation of bulk crystals, or film deposition from three elemental sources with independent rate control. It is important to note that the Curie temperature is independent of the composition, supporting the idea that a homogeneous alloy is the origin of the ferromagnetism. In total, three films were prepared at 600 °C, one with thickness 150 Å, and two with 2000 Å. All films showed the onset of ferromagnetism around 360 K as checked by MOKE. In the following we focus on SQUID magnetometry measurements obtained on one of the thick films, with field direction parallel to the film plane.

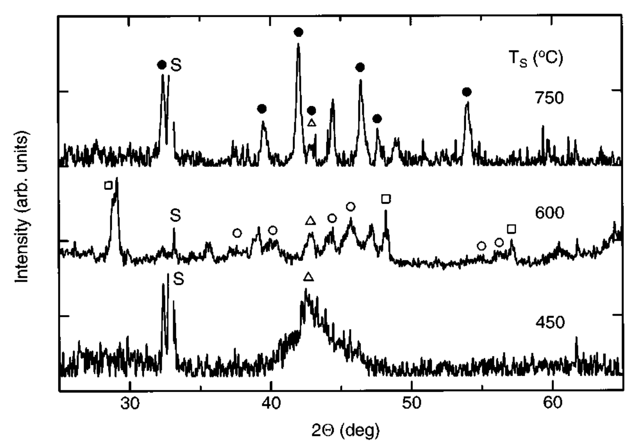

FIG. 1. $\theta/2\theta$ scans for 2000-Å thick Mn–Si–C films on Si (001) prepared at different substrate temperatures T_s. The background scattering from the vitreous silica substrate holder has been substracted for each scan. Symbols indicate reflections due to precepetation of Si (squares) and Mn (triangles), a Mn_5Ge_3-type structure (open circles) and a $Mn_{27}Si_{47}$ phase (closed circles). Substrate reflections are labeled ''S''.

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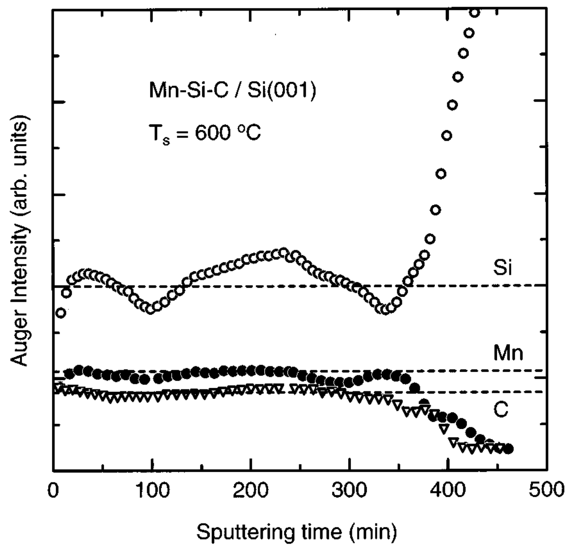

FIG. 2. Auger depth profile for a 2000-Å thick Mn–Si–C film. Dashed lines indicate the average signal for each element from which the composition was estimated. The Auger intensity change between maximum and minimum corresponds to a fluctuation of $\pm 5\%$ around the average Si concentration of 34%. The steep increase of the Si signal is due to the substrate after sputtering through the entire film.

Figure 3 shows the dc magnetization M (field-cooled) measured in an applied field of 10 Oe. The onset of ferromagnetism is seen at $T_c = (360 \pm 5)$ K with the error arising from the uncertainty of substracting the Curie–Weiss tail above T_c. The zero-field-cooled magnetization is essentially temperature independent and close to the zero line in this plot. Figure 4 shows three magnetization curves taken at 19, 150, and 320 K after substraction of the diamagnetic contribution of the Si substrate. The coercive field decreases monotonically with increasing T, as expected. M was measured up to 50 kOe at 19 K without evidence of an increase of M beyond the value acquired in 3 kOe. The saturation magnetization $M_s = 41$ emu/g at 19 K corresponds to about 0.55 μ_B/Mn atom, much smaller than the value of 2.5 μ_B expected for Mn. For Mn_5Ge_3 the saturation magnetization at 4 K was found to be 2.60 μ_B/Mn atom.[8] A definite conclusion concerning the ''missing moment'' is not possible because of the unknown volume fraction of the ferromagnetic phase.

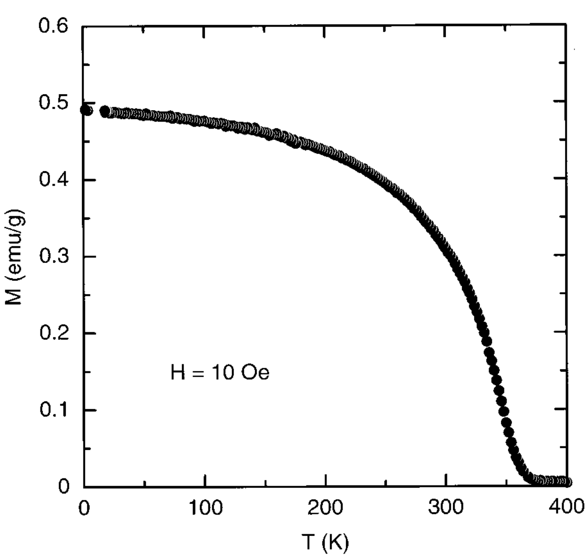

FIG. 3. Field-cooled dc magnetization M vs temperature T for a Mn–Si–C film ($T_s = 600$ °C) in an applied field $H = 10$ Oe.

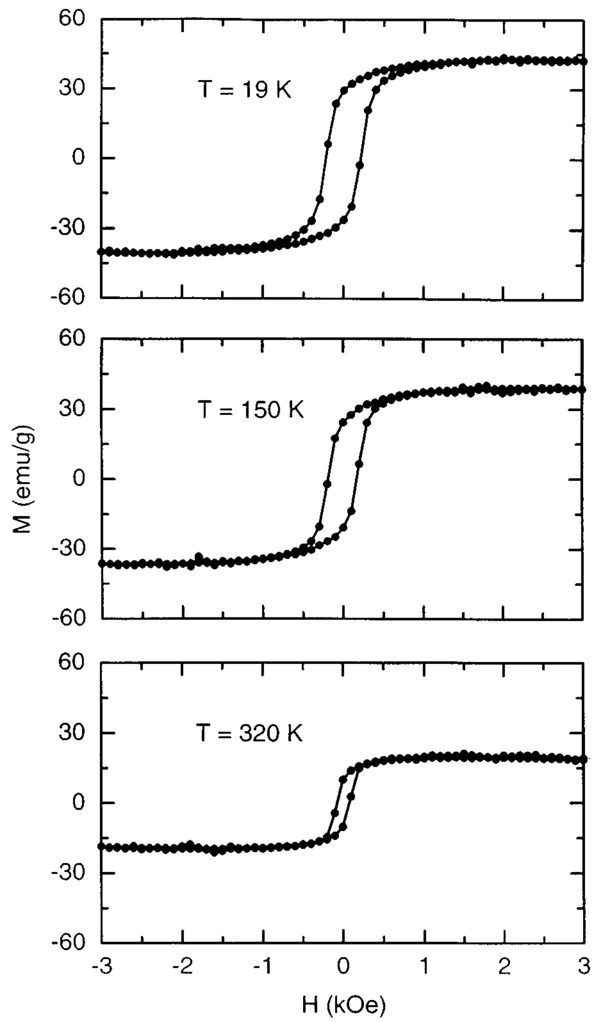

FIG. 4. Magnetization curves $M(H)$ of a Mn–Si–C film for different temperatures T.

In conclusion, we have prepared Mn–Si–C alloy films at 600 °C which are ferromagnetic with a well-defined Curie temperature of 360 K. To our knowledge, this is the highest T_c of any Mn-based alloy with the exception of the Mn/C/Si trilayers.[1] Further work is underway to elucidate the structural and magnetic properties of the alloys in more detail.

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