International Journal of Physics and Astronomy
June 2018, Vol. 6, No. 1, pp. 13-18
ISSN: 2372-4811 (Print), 2372-482X (Online)

Published by American Research Institute for Policy Development
DOI: 10.15640/ijpa.v6n1a1
URL: https://doi.org/10.15640/ijpa.v6n1a1

Growth and Magnetic Characterization of High Manganese Silicide Thin Films

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Abstract

Manganese silicide thin films have been successfully deposited by dc magnetron sputtering with Mn concentrations up to the high manganese silicide (HMS) range near $MnSi_{1.7}$. We observed the formation of a number of tetragonal crystallite phases, including Mn_4Si_7, $Mn_{27}Si_{47}$, and $Mn_{15}Si_{26}$, which are commonly referred to in the literature as near $MnSi_{1.7}$ or HMS; all of these phases have been confirmed using X-ray Diffraction. The formation of more HMS phases begin to appear at Mn concentrations around 29%, with XRD patterns clearly exhibiting the formation of the HMS phases with increased Mn concentrations. The low temperature saturation magnetization of these films increases with increased Mn concentration with a peak value of 100emu/cc for films near the $MnSi_{1.7}$ range. Films are paramagnetic at room temperature but start to exhibit ferromagnetism at low temperatures with the Mn concentrations around 35%, which corresponds to the $MnSi_{1.7}$ phases. Films close to $MnSi_{1.7}$ have a coercivity of about 300 Oe.

Keywords: thin films, magnetic materials, manganese silicide, magnetron sputtering

Introduction

There has been much interest in ferromagnetic semiconductors in recent years due to their application in the field of semiconductor spin transfer electronics (spintronics). Recent research in this field aims to use the increased spin degrees of freedom of charge carriers in semiconductors to increase the performance of electronic devices. Since traditional integrated circuits employ the charge in capacitors for memory storage, these ICs exhibit a volatile storage capability due to the loss of information when power is turned off or lost. Ferromagnetic materials, on the other hand, provide a non-volatile means of data storage. The addition of the spin degrees of freedom to the charge degrees of freedom in spintronic devices will provide the means for improved data processing speed, reduced power consumption and increased integration densities.

The dilute magnetic semiconductors (DMS) have be- come materials of choice in the area of spintronics. In some of the early work on DMSs, II-VI semiconductor alloys were doped with magnetic elements in the same way that p-type and n-type semiconductors are formed. However, the magnetic behavior of these compounds is dominated by the anti-ferromagnetic exchange of the Mn spins, resulting in either paramagnetic or anti-ferromagnetic behavior. [Ohno, 1998]

In another widely studied class of DMSs, a 3d-transition metal is used to dope a III-V semiconductor. One existing theory for these III-V DMS is based on the indirect exchange between the local magnetic moments, for example of the Mn interstitials, and the holes of the host. [Diehl et al., 2000; Takahashi et al., 2002; Dugaev et al., 2002; Inoue, 2003] Another theory suggests that the impurities such as Mn in the host provide localized and mobile holes near the top of the valence band, which play the role of unoccupied p-orbitals and thereby induce the ferromagnetism. [Fleuov et al., 2003] Silicon films with Mn concentration far beyond the DMS doping level are referred to as high manganese silicides (HMS).

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There has been much interest in the high manganese silicides near $MnSi_{1.7}$ over the past decade due to their possible use in applications ranging from thermoelectrics [Rebien et al., 2002; Teichert et al., 1996; Hou et al., 2005; Hou et al., 2007], to optoelectrics [Teichert et al., 1996; Hou et al., 2005; Hou et al., 2007; Gao et al., 2007], to photovoltaics [Rebien et al., 2002; Gao et al., 2007], and other silicon-based electronics applications. [Yang et al., 2001; Wang et al., 1997]

Among the 3d transition metal silicides, only $MnSi_x$ exhibits any ferromagnetic behavior. [Suplice et al., 2004; Gottlieb et al., 2003] Further, films with $x \sim 1.7$ exhibit the characteristics of semiconductors, whereas films with $x \sim 1$, are metals. [Hou et al., 2005; Wang et al., 1997] Thus, the ferromagnetic properties of the $MnSi_{1.7}$ phases have garnered further interest for use in spintronics applications as an ideal material to serve as spin injectors. [Stollenwerk et al., 2006; Krause et al., 2006; Mangano et al., 2006] The small lattice mismatch (~1.9%) between the HMSs and Si would enhance the epitaxial growth of thin films on the Si substrates. [Stollenwerk et al., 2006; Krause et al., 2006]

Typical methods of film growth for HMS thin films include evaporation of Mn onto Si substrates at temperature up to 1150° C [Adambaev et al., 2003] and with post-annealing [Hou et al., 2007], reactive growth of Mn on Si substrates with post annealing [Stollenwerk et al., 2006], molecular beam epitaxy [Rebien et al., 2002], ion implantation [Gao et al., 2007], and a modified Czochralski pulling technique [Gottlieb et al., 2003].

There are many advantages to magnetron sputtering, one of which is the versatility in target choices. We have used dc magnetron sputtering of a composite target to grow single-phase polycrystalline films at 400°C with a post-anneal at 500°C. The reason for the post-annealing rather than using a higher deposition temperature is that film growth at higher substrate temperatures resulted in an unstable plasma. The formation of the monosilicide MnSi has been widely reported to occur at ~400°C, whereas the phase transition to HMS has been reported to occur at annealing temperatures ~500°C. [Rebien et al., 2002; Wang et al., 1997; Stollenwerk et al., 2006] Thus, these growth and annealing temperatures are ideal for the formation of HMS thin films.

Also, the use of a composite target provides a more affordable alternative to other multi-magnetron systems, and allows for easy control of the film composition. Films synthesized by composite target sputtering were characterized for their compositional, structural and magnetic properties. We present evidence that HMS films prepared using composite target sputtering in the compositional range of ~35%, followed by annealing at ~500°C results in the formation of the crystalline phases of $MnSi_{1.7}$. Films prepared in this manner are easily reproducible and exhibit the ferromagnetic properties desirable for possible spintronics applications.

Experimental

All films were grown via dc magnetron sputtering of a p-doped Si target. Mn inclusion was accomplished by the addition of Mn chips to the target surface. The base pressure of the sputtering system was 5.0×10^{-6} Torr and sputtering was carried out in an Ar atmosphere with a flow rate of 30 sccm with an operating pressure of 10 mTorr. All samples were grown on quartz and (100) boron doped p-type Si substrates at a temperature of 400°C. The film growth rate was ~10 nm/min at 75 Watts DC power and films were approximately 150 nm thick. Film composition was determined by energy dispersive X-ray spectroscopy (EDS) using a FEI Quanta 400 electron microscope. Compositional data were determined using the $Si\ K_a$ and $Mn\ K_\beta$ peaks at 1.74 keV and 5.90 keV, respectively.

X-ray diffraction patterns were obtained at West Chester University on a Phillips Powder XRD using $Cu\ K_a$ radiation (0.15405 nm). Additional XRD were done at the University of Delaware using a Rigaku D-Max B Horizontal X-ray diffractometer with $Cu\ K_a$.

Magnetic behavior of the samples was determined using a Physical Properties Measurement System (PPMS) dc extraction magnetometer by Quantum Design Corporation. Measurements were performed with the field direction parallel to the film surface.

Results & Discussion

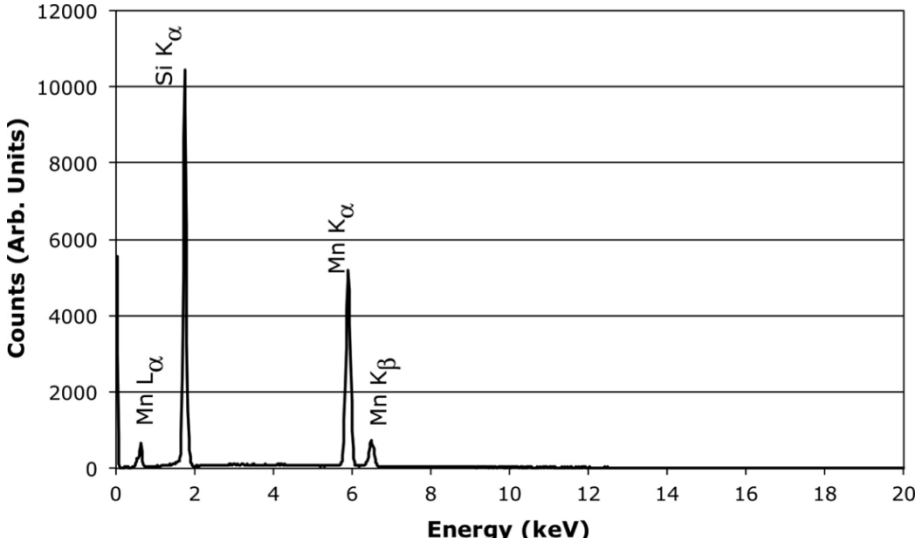

Figure 1. The EDS Spectrum for $MnSi_{1.7}$ film.

Structural Properties

The film composition ranged from 0 to 41 atomic % Mn. Fig. 1 shows an EDS spectrum for a film with 29% Mn. SEM micrographs indicate that the films were smooth and continuous as can be seen in Fig. 2. The structural properties of pure and Mn doped Si films were obtained using X-Ray Diffraction (XRD). Fig. 3 shows the XRD patterns from films with Mn contents ranging from 0% to 35%. The 0% sputtered film was pure Si film deposited at 400° C and post-deposition annealed at 500° C in vacuum. This annealing temperature was chosen because of the reported formation of monosilicide MnSi around 400° C, as mentioned earlier. [Rebien et al., 2002; Wang et al., 1997; Stollenwerk et al., 2006]

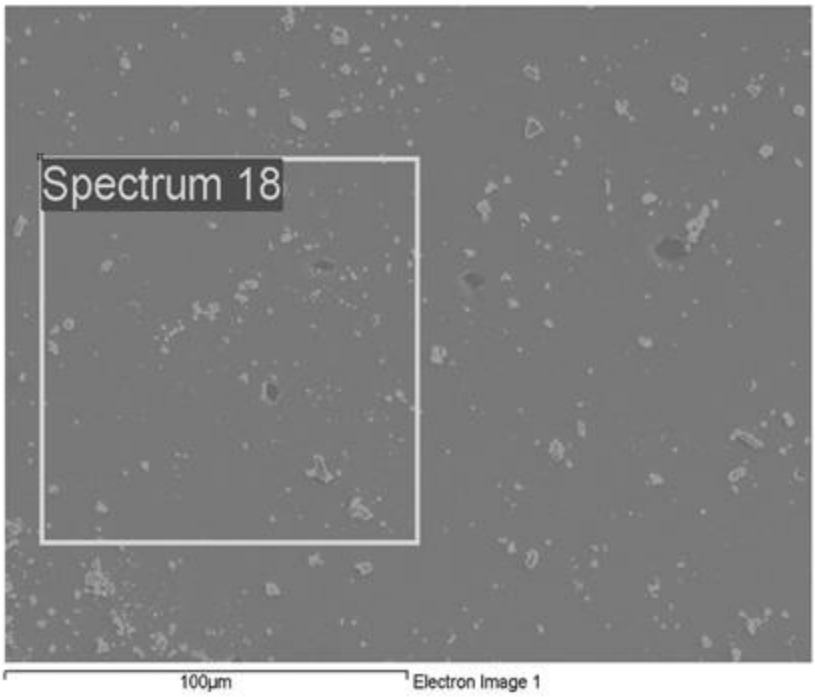

Figure 2. SEM Micrograph for a $MnSi_{1.7}$ film.

All films were annealed in the same way. No XRD peaks were observed in the 0% of 10% Mn annealed films. The 29% Mn annealed film begin to show structure as peaks at 26.0 and 47.7 start to appear. These peaks grew in intensity with further addition of Mn to the Si, with the 35% Mn sample showing well-defined XRD peaks. The peak at 26.3 corresponds to the (101) reflection from the quartz substrate. The peaks at 26.0 and 47.7 correspond to the (104) and (222) reflections of the tetragonal phase Mn_4Si_7. It should be noted that these peak positions also closely match the (1 0 27) and (1 1 54) reflections for $Mn_{27}Si_{47}$, and the (1 0 15) and (1 1 30) reflections for $Mn_{15}Si_{26}$ phases, respectively.

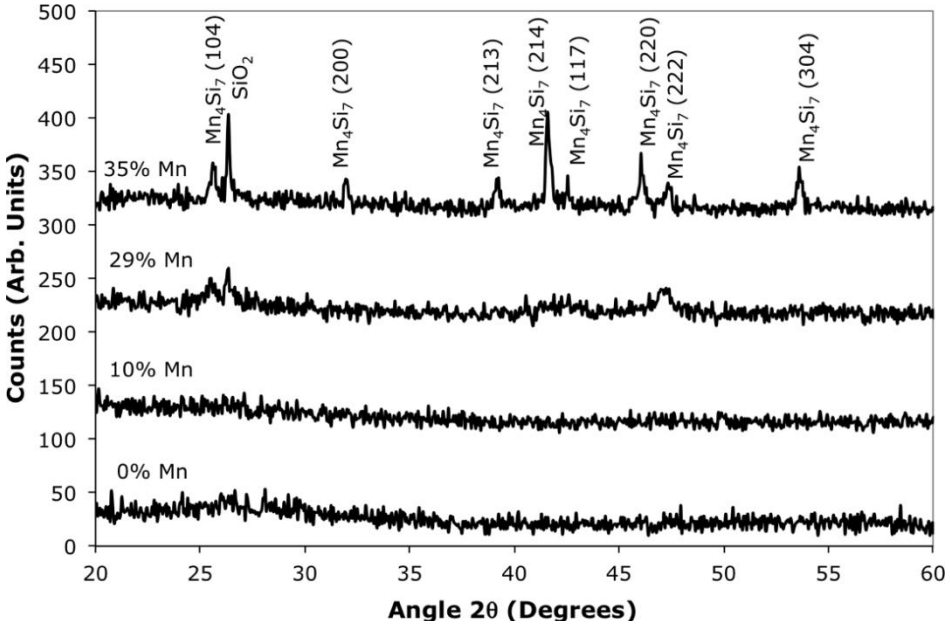

Figure 3. XRD Pattern of selected $MnSi_x$ films annealed at 500°C.

The primary structural difference between these tetragonal phases being the c lattice parameter. All of these phases have similar lattice parameter a, and the c values are multiples of 0.4367 nm, Mn_4Si_7 has c=1.746 nm, $Mn_{27}Si_{47}$ has c=11.79 nm, and $Mn_{15}Si_{26}$ has c=6.531 nm. [Mahan et al., 2004] These phases will be referred to as $MnSi_{1.7}$ in the following discussion. As the Mn concentration is increased, we first observe the $MnSi_{1.7}$ phase in films with 29% Mn. Since the $MnSi_{1.7}$ phase corresponds to a 35% Mn film, this suggest that there will still be some pure Si phase present in the films. However, XRD does not detect this phase. This could be due to the amorphous nature of the Si phase. It has been reported in the literature that the Si crystallizes between 600° C and 750° C depending on annealing time, therefore, we do not expect to see any XRD peaks related to the pure Si phase. [Muraca et al., 2008] Further identification studies need to be performed to confirm this assumption. With an increase in Mn concentration, we see an increase in the peak intensities as well as appearance of other weaker XRD peaks of these phases. At 35% Mn in Si, which closely matches $MnSi_{1.7}$, the 8 strongest peaks in our XRD pattern match closely in position and intensity with HMS phases near $MnSi_{1.7}$, indicating the formation of HMS. All of these phases mentioned above (Mn_4Si_7, $Mn_{27}Si_{47}$, and $Mn_{15}Si_{26}$) give XRD peaks that closely overlap each other, which made an exact determination of the phase difficult. No single phase is explicitly specified. [Wright et al., 1981; Karpinsky, 1969; Zwilling et al., 1973; Knott et al., 1967] The average grain size, calculated from Scherer's formula, is about 35 nm.

Magnetic Properties

Although at room temperature we have not observed a clear ferromagnetic behavior, low temperature magnetization measurements, done at 5K, have shown that films are ferromagnetic. Suplice et al. reported a Curie temperature of $T_c = (43\pm1)$ K for the weak itinerant magnetic system of Mn_4Si_7. [Suplice et al., 2004] The magnetic hysteresis loops shown in Fig. 4 were obtained at 5K after cooling the films in zero magnetic field. As expected, the increasing Mn concentration resulted in an increased saturation magnetization of the films along with an increased coercivity. The magnetization appears to reach saturation at around 1000 Oe (0.1 T) regardless of Mn concentration. However, the remanent magnetization increased significantly from about 40 emu/cc to above 100 emu/cc as the Mn concentration is raised from 17% to 35%.

This is coupled with a significant increase in the coercivity to ~300 Oe as well. The low ratio of remanence to saturation magnetization, M_r/M_s, of 0.08 in the 17% sample is due to uniform distribution of Mn atoms in the Si matrix.

On the other hand, the high M_r/M_s ratio of 0.34 observed in the 35% sample indicates that increased Mn concentrations promotes exchange interactions between the Mn atoms. Typically, exchange interactions between neighboring Mn atoms are expected to favor domain formation with anti-parallel neighboring domains in order to decrease the magneto static energy of the system at the expense of decreased coercively. Since the coactivity and remanence of the 35% Mn sample both increase as compared to the lower concentration samples, it can be concluded that the domains are not close enough to each other to form the reversed or anti-parallel domain structure.

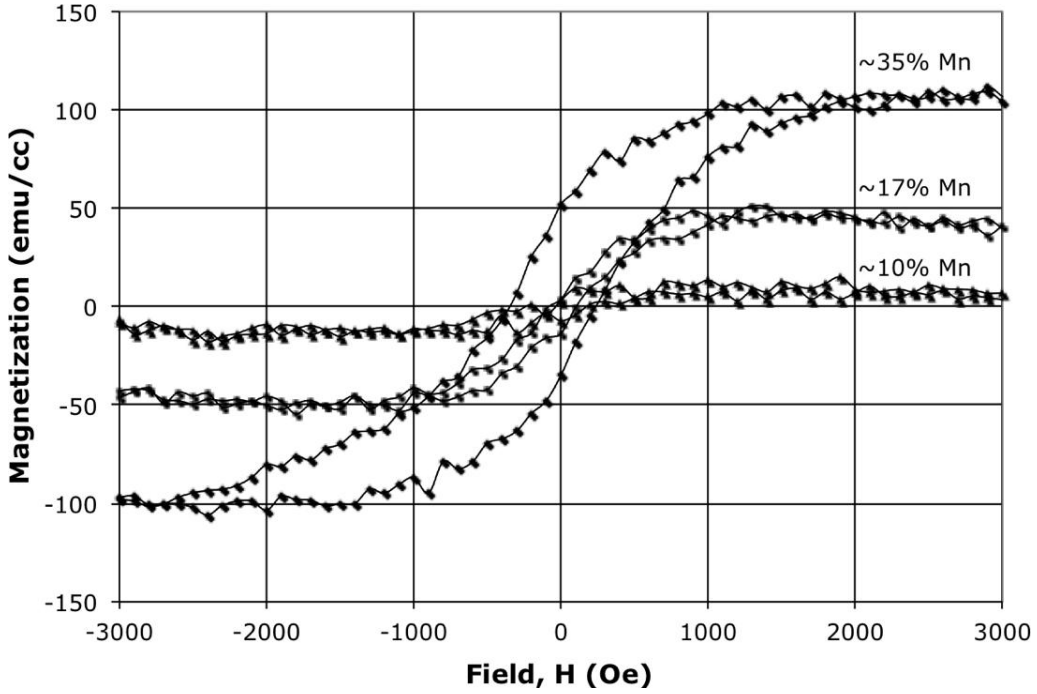

Figure 4. Zero field cooled M-H hysteresis curves for samples with various Mn concentrations.

Conclusions

We have successfully deposited high manganese silicide thin films with concentrations ranging up to 35% Mn in Si using dc magnetron sputtering from a composite target followed by an annealing at 500 C. Upon annealing, these films exhibit the characteristic XRD patterns of the tetragonal phases of $MnSi_{1.7}$. A definitive determination of the exact phase present has not been made due to many similar tetragonal phases near the 1:1.7 ratio, including Mn_4Si_7, $Mn_{27}Si_{47}$, and $Mn_{15}Si_{26}$. These phases all have the same a lattice parameter, but different c lattice parameters, which are all multiples of 0.4736 nm. These films exhibit paramagnetic behavior at room temperature, but are ferromagnetic at low temperatures. HMS films close to the $MnSi_{1.7}$ structure exhibit a high saturation magnetization of about 100 emu/cc and a coercivity of ~300 Oe. These results indicate well-separated magnetic domains in the HMS films, which is desirable for such applications as spin-injector for spintronics.

Acknowledgements

The authors would like to acknowledge and thank Abdullah Ceylan, Abdul Rumaiz and Sadan Ozcan for their help in acquiring the magnetic and structural data at the University of Delaware.

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