Combinatorial Synthesis and Characterization of CoMnGe Alloys

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ABSTRACT

Ternary alloys of CoMnGe have been synthesized and characterized using combinatorial molecular beam epitaxy techniques. Structural evolution was studied using real-time scanning reflection high-energy electron diffraction, and magnetic properties were probed using magnetooptic Kerr effect imaging and SQUID magnetometry. Growth and properties on several substrate orientations were explored. These alloys exhibit a rich variety of magnetic and magnetooptic behavior, including a robust phase near Co2MnGe with high spin polarization, Tc, and magnetooptic response. The observed magnetic responses show strong correlation with structural transformations, such that structural ordering leads to enhanced magnetism. The observed magnetic behavior and the alloys’ compatibility with Ge and Si substrates make them potential candidates for spin electronic transport studies and applications.

INTRODUCTION

Magnetic alloys are fundamentally interesting and technologically important, because they offer a wide range of novel structures and properties that are not present in elemental materials, including magnetic semiconductors,1 half-metals,2 bulk metallic glasses.3 Heterostructures of these systems may provide key materials systems for the development of new magnetic device concepts. The exciting prospect of studying these materials is to be able to tailor experiments in order to explore specific properties, such as specific structure-property relationships. However, the large number of combinations and the nontrivial composition dependent structural and magnetic phase diagrams have also made them difficult to study, particularly using the traditional one sample at a time approach that is not only tedious and time consuming but also not sensitive to abrupt changes and phase boundaries. New approaches and techniques are necessary for exploring these systems systematically, so that properties can be screened rapidly and efficiently and intricate interactions between structures and properties can be elucidated. In this paper we describe application of combinatorial approach to conventional molecular beam epitaxy (MBE) synthesis and characterization of multicomponent alloys, and we use a ternary film system, CoMnGe, as an example to illustrate the approach and to highlight what can be done with it. The alloy system is chosen because novel half-metallic ferromagnetism has been predicted in it 2 and its potential compatibility with standard semiconductor substrates. In the following sections we first describe combinatorial MBE synthesis and characterization, particularly the approach of “continuous phase diagramming” (CPD), and then present some of our findings on epitaxial films of CoMnGe grown on Ge.

COMBINATORIAL SYNTHESIS AND CHARACTERIZATION

Combinatorial synthesis was carried out using an advanced MBE system. A combination of computer controlled sample rotation, masking, and source shutters was used to execute the
combinatorial synthesis. A linear gradient thickness profile (wedge) for each of the precursors, i.e. Co, Mn, Ge, was produced during deposition by moving a precision shadow mask across the substrate. The orientation of each linear profile in the plane of the substrate, say 120° apart, was established by sample rotation before each deposition. Each precursor was deposited sequentially to form a monolayer or submonolayer trilayer at a chosen growth temperature, and the trilayers were repeated to produce a thick film. The sequence of deposition of different precursors can be chosen to promote epitaxial growth of certain phases. In general the use of the multilayer method can give an extra dimension for producing metastable or unstable alloys, particularly imposing an artificial stacking sequence along the growth direction. The real-time epitaxial processes were monitored by a 30 kV Staib/kSA scanning reflection high-energy electron diffraction (RHEED) CCD imaging and analysis system. Co and Ge were evaporated from e-beam hearths, and Mn from an effusion cell, with growth rates maintained at about 0.1 Å/s. Deposition rates were monitored using a quartz crystal monitor and calibrated *ex-situ* by using a profilometer and Rutherford backscattering spectroscopy (RBS). Growth temperatures between 100 and 400 °C and post growth annealing were studied. The processing steps studied were aimed at optimizing epitaxial growth of particular phases. Films of the complete ternary combinatorial libraries, i.e. $\text{Co}_x\text{Mn}_y\text{Ge}_{1-x-y}$, and linear libraries sliced through the ternary system, e.g. $(\text{Co}_{1-x}\text{Mn}_x)_1-a\text{Ge}_a$, were produced. Magnetooptic Kerr effect (MOKE) imaging and SQUID magnetometry were used to study the magnetic phase diagram. Field and temperature dependences were measured.

**RESULTS AND DISCUSSION**

Other than a few magnetic compounds, including $\text{Co}_2\text{MnGe}$, which is predicted to be fully spin polarized at the Fermi level, the phase diagram of CoMnGe is largely untapped. Our experiments show that this ternary system exhibits rich structural and magnetic behavior. The robust magnetism is illustrated in figure 1 by room temperature differential MOKE intensities of a 250 Å complete ternary combinatorial library grown on Ge (001) at 150 °C and annealed at 350 °C. The transverse differential MOKE intensity shown in figure 1 was measured at ±5 kOe using a 12-bit CCD camera, i.e. $\Delta I = I(5 \text{ kOe}) - I(-5 \text{ kOe})$, so it corresponds mostly to the saturated states. Areas of high intensity correspond to magnetic regions at room temperature with strong magnetooptic coupling. Conversely, areas of suppressed intensity are nonmagnetic regions. The boundaries of these regions when combined with further examinations of the field dependence, particularly the remanent states yield the contour of room temperature phase diagram of the system. This system has many strongly magnetic regions, including most notably doped Ge, doped Mn, and near the middle of the phase diagram where the MOKE response is very strong. When these experiments are carried out at various temperatures, temperature dependent magnetic phase diagrams can be built up by the isothermal contours of phase boundaries. For instance high $T_c$ materials can be identified, as the magnetic regions shrink with increasing temperature. Further examinations of the system have shown that the Curie temperature and magnetic moment of the middle ferromagnetic regions are very high, with regions perhaps comparable to or even more robust than those of Co and Fe. Magnetic anisotropy is another important property that can be mapped quantitatively by using MOKE imaging as a function of amplitude and orientation of the field, from which critical fields are determined, e.g. saturation field $H_s$ and coercive field $H_c$. One example is shown in the inset of figure 1 for the composition dependent coercivity at room temperature. From this, hard and soft magnetic regions can be identified and studied.
In order to explore the magnetism and structure further, linear libraries, such as \((\text{Co}_x\text{Mn}_{1-x})\text{Ge}_{1-a}\), were synthesized and characterized. Figure 2 shows one such set of measurements for \((\text{Co}_x\text{Mn}_{1-x})_0.8\text{Ge}_{0.2}\) grown on Ge (111) at 150 °C. As shown in figure 2, structure and magnetism exhibit strong correlations. In particular high MOKE intensities coincide with structural orders, as they are indicated by high RHEED intensity and narrow width. In general MOKE intensity has slightly different power dependence on magnetization in different materials, and it can be quite sensitive to the symmetries of electronic and crystalline structures. Therefore, it is not surprising to find a Kerr anomaly at a structural phase transition. The sharp asymmetric cusp-like peaks in RHEED intensity near \(x = 0.65\) and 0.95, and the corresponding sharp changes in lattice constants are very close to the known compounds of \(\text{Co}_2\text{MnGe}\) and \(\text{Co}_3\text{Ge}\), respectively, both in composition and in lattice parameters. For instance, the observed lattice constants near \(x = 0.65\) are very close to the published value of \(\text{Co}_2\text{MnGe}\), which is ~ 1.5 % greater than that of Ge. The as-grown structures for \(x < 0.6\) are highly disordered, as they are indicated by the low RHEED intensity and high diffused scattering in the middle of figure 2. However, at Mn-rich end with \(x < 0.2\), annealing at above 200 °C can produce highly ordered epitaxial structures, which also coincide the observed antiferromagnetic behavior. Similar behavior was observed for growth on Ge (001), indicating that the ordered phases in this region have 3 dimensional epitaxial relationships with Ge. The growth of the ordered phases is consistent with that of a strained system. Pseudomorphic growth for the first one or two atomic layers is followed by a transition to 3 dimensional growth signaled by a drop in specular intensity and the subsequent rise in

![Figure 1. Room temperature magnetic phase diagram of a 250 Å CoMnGe combinatorial library grown on Ge (001) by MBE. Top: image of differential MOKE intensity measured at ±5 kOe, i.e. \(\Delta I = I(5 \text{ kOe}) - I(-5 \text{ kOe})\). Bright areas correspond to the magnetic regions. The respective directions of field and light polarization were along the vertical and horizontal. Bottom: coercivity of the lower right hand portion (box) of the sample (top). The numbers to the right of the gray scale bar indicate the coercive field strength in Oe.](image)
diffraction intensity and the corresponding change in the in-plane lattice spacing. The different onsets of ordering also reflect the corresponding complexity of lattice stacking sequences, thus different sizes of unit cells. The RHEED data shown in figure 2 are those obtained after the deposition of each Co-Mn-Ge trilayer with Ge on top, and more detailed analyses of the RHEED during the trilayer deposition show that among the three elements Co appears to stabilize the ordered structures in this region, as it is illustrated in figure 3 for growth near a composition of Co$_2$MnGe along (111) at 300 °C. This tendency is indicated by the systematic increase of RHEED intensity and decrease of width during deposition of each Co layer, and the reversal during deposition of other components. This finding demonstrates the usefulness of using sequential deposition to stabilize particular alloy structures.

**Figure 2.** Structural evolution and magnetism of (Co$_x$Mn$_{1-x}$)$_{0.8}$Ge$_{0.2}$ library grown on Ge (111) as a function of Co concentration x (horizontal axes). Top: Transverse differential remanent MOKE intensity at room temperature. RHEED intensity (middle) of the 0$^{th}$ order reflection and in-plane lattice spacing ratio (bottom diagram) between the film and Ge substrate as a function of thickness (vertical axes) for growth at 150 °C. The RHEED data shown here were measured after the completion of each Co-Mn-Ge trilayer with a nominal thickness of 2 Å.

As indicated above, evolutions of epitaxial growth of the alloy system exhibit many interesting phenomena, arising from strain and ordering of the components among others. The application of combinatorial approach makes it possible to explore these. Figure 3 shows one example of the alloy epitaxial growth along the (111) direction, where the RHEED specular intensity undergoes various transitions and oscillations. The specular intensity measures directly the ordering and smoothness of the surface. In other words high intensity corresponds to a chemically ordered and atomically smooth surface.
Figure 3. Evolution of $0^{\text{th}}$ order RHEED intensity near a composition of $\text{Co}_2\text{MnGe}$ as a function of time for MBE growth along (111) on Ge (111) at 300 °C. Each trilayer of $\text{MnCo}_2\text{Ge}$ is about 1 Å thick and grown in 40 s, or about 25 trilayers in 1000 s. The spikes on the curve correspond to oscillations induced by the sequential submonolayer trilayer growth. Inset is a zoomed-in region indicated by the gray box, in order to show the details of the oscillation. Specifically the rise corresponds to Co deposition and the fall the Mn and Ge depositions. The flat regions (e.g. the one around 700 s in the inset) correspond to periodic pauses, programmed for the sequential deposition, typically every 5 trilayers for this growth.

SUMMARY

Combinatorial MBE techniques have been used to explore structure and magnetism of epitaxial films of magnetic CoMnGe alloys. These alloys exhibit a rich variety of magnetic and magnetooptic behavior, including a robust phase near $\text{Co}_2\text{MnGe}$ with high polarization, high $T_c$ and high MOKE response. The observed structure and magnetism are intertwined, such that enhanced magnetic responses are shown to correlate with structural transformations. Specifically, structural ordering and change of symmetry are shown to give rise to enhanced magnetic and magnetooptic interactions. The observed robust magnetism in these alloys and their compatibility with Ge substrates make them excellent candidates for spin electronic studies and applications. The key challenge is to elucidate these phenomena, and combinatorial MBE provides the necessary means to do this. From a broader perspective, this article is intended to illustrate that the true strength of combinatorial approach lies in the ability to probe narrow states and transitions systematically. However, systematic experiments still need to be carefully designed so that intrinsic phenomena can be targeted and examined, and they should not be used as “shotgun” approach.
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