Electrical properties of epitaxial $Cr_{100-x}Co_x(100)$ alloy thin films on MgO(100)

Abstract. Cr-Co alloys and Cr/Co multi-layered systems have shown considerable promise in practical applications because of its Invar-like properties and enhancement of the SDW, respectively. Comparison between Cr in bulk and thin film forms revealed dimensionality plays an important role in modifying the SDW structure. Epitaxial $Cr_{100-x}Co_x$ thin films of thickness (t) ≈ 200 nm, with $0 < x < 7.2$, were prepared on MgO(100) substrates using DC magnetron co-sputtering techniques. The resistivity (ρ) for these samples was measured in the temperature range 2 K < T < 395 K and used to determine the Néel transition temperatures (T_N) for the individual samples. The T_N versus x plot for this sample series shows non-monotonic behaviour and sheds light on the effect of dimensionality on the electrical properties of the Cr-Co alloys.

1. Introduction

In the entire 3d-series, only chromium and manganese exhibits antiferromagnetic ordering [1]. The temperature dependence of the magnetic structure of chromium below the Néel temperature (T_N) is characterized by a longitudinal (L) or transverse (T) spin density wave (SDW), with wave vector $\bar{\boldsymbol{Q}}$, that is incommensurate with the period of the reciprocal lattice [2]. The Néel temperature, T_N = 311 K, is well established for bulk chromium. Comparison between Cr in bulk and thin film forms indicated that dimensionality plays an important role in modifying the SDW structure [3].

Recent studies revealed that Cr alloys with group-8 magnetic transition metals such as Fe, Co and Ni show magnetic phase diagrams quite different from each other [2]. However, some similarities are observed with individual doping of Fe and Co into a Cr host. Firstly, doping with both metals exhibits a triple point, where the incommensurate (I) spin density wave (SDW), commensurate (C) SDW and paramagnetic (P) phases converge [2]. Secondly, with doping these metals, initially T_N decreases slowly up to certain electron concentration and then increases with increasing electron concentration [2]. Shibatani [4] and Moyer *et al*. [5] explained this anomalous behaviour in T_N considering the interaction between local moments and the SDW host. In Cr-Co alloys, Co local moment is strongly coupled to SDW [6]. Hence, unlike in pure Cr, it is expected that dimensionality in Cr-Co alloys should have strong effect on SDW structure. Interestingly, Ge *et al*. [7] reported that at a certain layer thickness, the SDW in Co/Cr multilayers have been enhanced as compared to bulk Cr-Co alloy system

Besides interesting antiferromagnetic properties, Co-Cr alloys have numerous applications. Co-rich Co-Cr alloy thin films have been studied extensively for their applications in a recording and storage media [7, 8]. Ferromagnetic Invar and Elinvar type alloys are widely used in the field of

electromagnetic and precision instrumentation engineering [9]. Their use is often limited due to their ferromagnetism, as these alloys cannot be used in electromagnetic and precision instruments which are used in a static magnetic field. Also, in alternating magnetic field these alloys exhibits a magnetostrictive oscillations [9]. Another drawback of these alloys is that the elastic moduli of ferromagnetic Elinvar type alloys are affected remarkably in magnetic fields. However, Cr-Co alloy system is of considerable practical importance because of its both Invar and Elinvar properties along with non-ferromagnetism [9].

The magnetic phase diagram for Cr-Co alloys with lower concentrations of Co is well established [2], but effect of dimensionality on the magnetic phase diagram is yet to be explored. Therefore, taking this into consideration, the present paper studies the effects of thin-film growth and dimensionality on the magnetic phase diagram and electrical properties of Cr-Co alloys.

2. Experimental

Epitaxially-grown $Cr_{100-x}Co_x$ thin films of thickness (t) ≈ 200 nm, with $0 < x < 7.2$, were prepared on MgO(100) single-crystal substrates using DC magnetron co-sputtering techniques. Structural studies of these samples were carried using X-ray diffraction (XRD) techniques (Phillips PAN analytical X-pert Pro X-ray diffractometer) in the 2θ range 20–100° using Cu-$K_{\alpha 1}$ radiation (λ = 1.54056Å). The XRD patterns were compared with standard Joint Council of Powder Diffraction Database (JCPDD) files of Cr (06-0694). The electrical resistivity (ρ) measurements for these films were carried out in the temperature range 2 K < T < 395 K using a Quantum Design Physical Properties Measurement System (PPMS), using the standard four probe technique. For resistivity measurements, the electrical current was directed along the [100] direction. The electrical resistivity measurements were employed to determine Néel temperature for the individual films.

3. Results and Discussion

Figure 1 shows a representative XRD result for the $Cr_{100-x}Co_x$ thin films with x = 1.3, prepared on a MgO(100) substrate. The result indicates that the sample is indeed epitaxial, exhibiting a single crystallographic orientation, with preferred [100] growth direction. The additional peaks observed in XRD patterns are due to the substrate contribution.

The electrical resistivity $\rho(T)$ curves for $Cr_{100-x}Co_x$ thin films, with $0 < x < 7.2$, are shown in Figure 2 (a) to (d). Well defined anomalies in the form of domes are observed in ρ (T) curves of all the thin films. The hump like anomaly in each of the resistivity of the $\rho(T)$ curve of the thin films are attributed to the formation of SDW on entering the antiferromagnetic phase on cooling through the Néel temperature (T_N) [2]. This anomaly observed below T_N, finds its origin in the nesting of electron and hole Fermi surfaces [2], which indicate the decrease in the number of charge carries available for the conduction below T_N. The actual determination of T_N is discussed further in the text. Generally, exciton formation takes place in Cr-Co alloys during transition from paramagnetic to antiferromagnetic state below T_N. Hence these alloys can be treated as exciton dielectrics [1, 10]. According to Anderson's model of localized states in metals [1, 11], the d-d repulsion energy is higher than the s-s and s-d repulsion energy. Since Co exhibits local moments, a d–shell state on Co impurity atom of spin up is full while spin down is empty. Due to repulsion energy in d–shells an electron with spin down will experience extra repulsion compared to the spin up electron. Thus, the spin up state energy level ($E_{d\uparrow}$) lies below the Fermi level (E_F) and hence transition of electrons to $E_{d\uparrow}$ increases the resistivity over wide temperature range below T_N [1]. From Figure 2, the rise in resistivity below T_N, is found to be more pronounced for the films with x = 6.4 and x = 7.2 as compared to the films with x < 6.4. This indicates the enhancement of SDW in these alloy thin films. Ge *et al*. [7] and Antonoff [12] attributed such behaviour to originate from the interaction between the Co moments and the SDW.

An additional anomaly, the minimum in resistivity below approximately 75 K, is observed for the films with x = 6.4 and x = 7.2 as seen in Figures. 2 (c) and (d), respectively. An analogous resistivity minimum observed in Cr alloys at low temperature has been investigated [14] and was originally

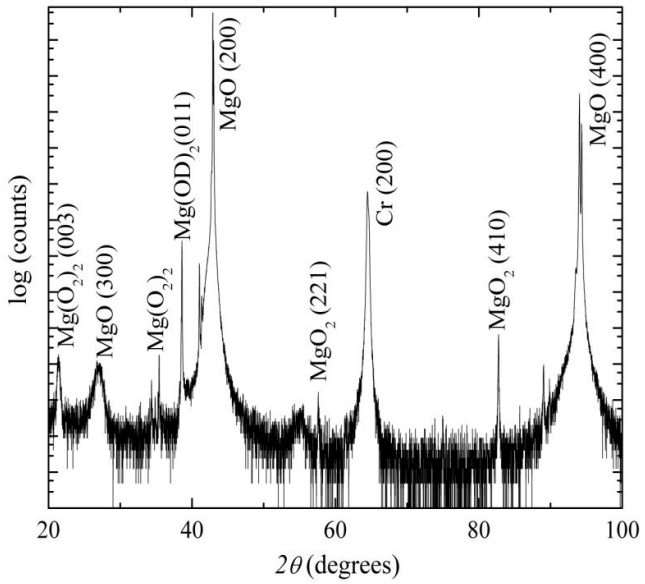

Figure 1. θ-2θ XRD scan (Bragg-Brentano geometry) in which the scattering vector is maintained normal to the plane of the film, for $Cr_{100-x}Co_x$ thin films with x = 1.3, prepared on MgO(100) substrate.

attributed to the Kondo effect [13, 14]. Magnetic susceptibility measurements on Cr-Co alloys system showed that Co have a local moment in Cr alloys [6]. However, the observed susceptibility behaviour of Cr-Co alloys does not satisfy the Curie-Weiss law at low temperatures, indicating that the Co local moment is strongly coupled to the SDW [6]. Generally, the presence of a local moment in metallic host leads to a situation favourable for the Kondo effect [6, 15]. However, in magnetically ordered systems the exchange field suppresses the Kondo state, but interestingly the low temperature minima is pronounced in Cr-Co alloys in their ordered state [6]. Kondorskii *et al.* [1] also suggested that to attribute the low temperature resistivity minimum (T_{min}) to Kondo-type behaviour the relation, $\rho \sim \ln T$ should hold below T_{min}. They observed that in bulk Cr-Co alloys with Co impurities in the range 4 at.% to 8 at.%, resistance minimum satisfies $\rho \sim (T)^{1/2}$ relation rather than $\rho \sim \ln T$ relation and discarded the possibility to attribute this resistivity behaviour below T_{min} to Kondo-like resistance minimum. The $\rho \sim (T)^{1/2}$ dependence of resistivity below T_{min}, is explained by taking into account the inelastic electron-electron interaction and the elastic scattering of electron by the impurities [1]. Also, Katano *et al.* [13] suggested that the Kondo effect causes the resistivity minimum in Cr-Co alloys with commensurate SDW state. The view that the resistance minimum is Kondo-type behaviour was questioned by Fawcett *et al.* [2].

In the present investigations, the detailed $\rho(T)$ data analysis for films with x = 6.4 and x = 7.2, revealed that resistivity behaviour below T_{min} does not obey the $\rho \sim (T)^{1/2}$ nor the $\rho \sim \ln T$ relation up to 2 K. The insets in Figure 2 (c) and (d) shows clear non-linear behaviour in ρ vs $\ln T$ plots for the alloys with x = 6.4 and x = 7.2. It should be noted that experiments done by Kondorskii *et al.* [1] were carried out on bulk Cr-Co alloys down to 4 K below T_{min}, while the experiments reported here are done on Cr-Co thin films down to 2 K. Considering the current ρ versus $\ln T$ results it appears that a linear region can be found in the temperature range 44 K < T < 12 K corresponding to the work of Kondorskii *et al.* [1], but it deviates for T < 12 K.

Boekelheide *et al*. [16] studied the electrical resistivity of Cr thin films and observed the low temperature resistivity minima analogous to that observed in Cr-Co alloy thin films in our experiments. They stated that the minimum was attributed to the impurity resonant scattering (IRS). This conclusion was supported by the following: firstly, the specific heat measurements on the Cr thin films showed large density of states at Fermi level and secondly, the SDW suppressed the spin-flip scattering of the conduction electrons [16]. However, to confirm that T_{min} in the present Cr-Co films is attributed to IRS specific heat measurements on these films should be done.

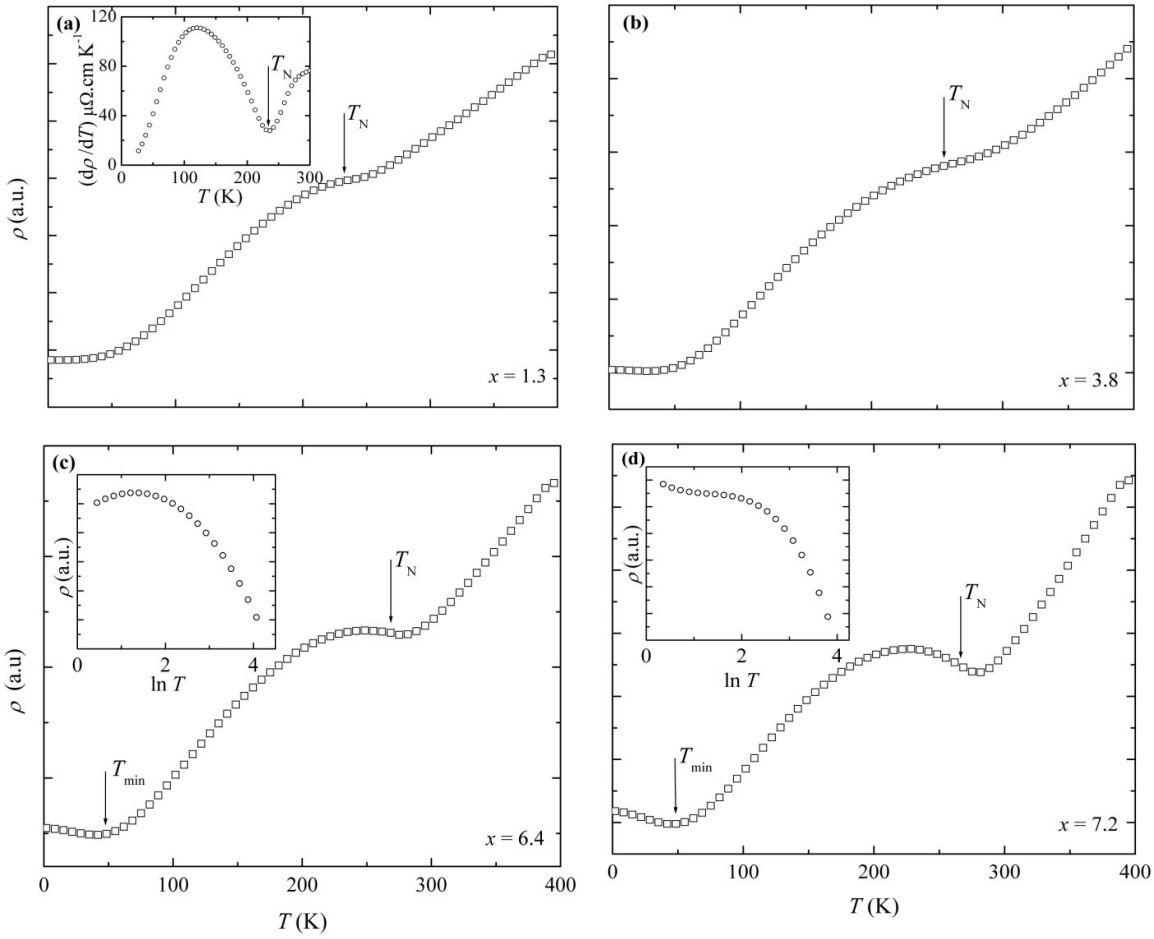

Figure 2. The resistivity (ρ) as a function of temperature (T) for $Cr_{100-x}Co_x$ thin films: (a) x = 1.3, (b) x = 3.8, (c) x = 6.4 and (d) x = 7.2. The arrows indicate the position of the Néel temperature (T_N) obtained from minimum in dρ/dT versus T plots for all the samples. Insets show dρ/dT versus T plot for (a) x = 1.3 and the ρ vs ln T plots for (c) x = 6.4 and (d) x = 7.2.

In the case of Cr alloys T_N can be defined in one of the two ways: either as the temperature of minimum in d$\rho(T)$/dT accompanying magnetic phase transition [2] or T_N is defined at the inflection point of the $\rho(T)$ curve. In this study the second approach was followed because of the broadened transition often observed in films. In order to determine the T_N, dρ/dT versus T plots for all Cr-Co thin films were considered and T_N was taken as a temperature associated with the minima on the corresponding plot. A representative plot used to determine T_N for $Cr_{100-x}Co_x$ thin films with x = 1.3 is shown in the inset of Figure. 2 (a). The obtained T_N values are denoted by the arrows in the corresponding Figures 2 (a) to (d). The variation of T_N as a function of x for $Cr_{100-x}Co_x$ thin films is shown in Figure. 3. It is seen that T_N decreases with doping up to 2.6 at.% Co. Further T_N increases rapidly for doping up to 6.4 at.% Co reaching a maximum and then decreases. This is in agreement with the dependence of T_N non-monotonically on cobalt densities, obtained from neutron diffraction studies on bulk materials [1, 17]. In case of Cr-Co system in bulk form, the triple point (L) is observed for triple point concentration (x_L) 1.3 at.% Co concentration at triple point temperature (T_L) 280 K [2]. However, from Figure. 3, it is seen that in the case of epitaxial Cr-Co thin films, L appears to be

Table 1. Comparison between Néel temperature (T_N) for bulk and thin film form of $Cr_{100-x}Co_x$ alloy with different values of x.

$Cr_{100-x}Co_x$ alloy with x	T_N, K for Cr-Co alloy in Bulk form [2]	T_N, K for Cr-Co alloy in thin film form
1.3	281	234 ± 2
2.6	319	222 ± 3
2.9	320	233 ± 3
3.8	317	259 ± 2
6.4	290	268 ± 1
7.2	286	258 ± 2

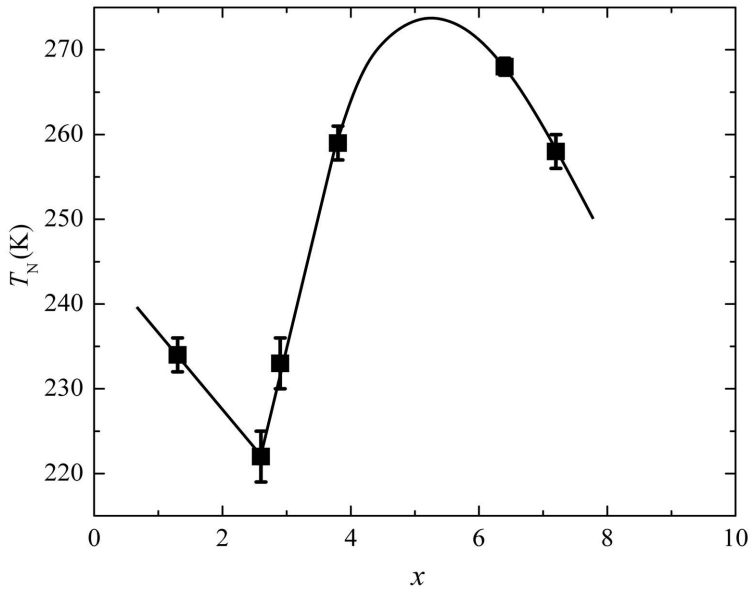

Figure 3. The Néel temperature (T_N) as a function of x for the epitaxial $Cr_{100-x}Co_x$ thin films prepared on MgO(100).

shifted to x_L = 2.6 and T_L decreased to 222 ± 3 K. Table 1 shows comparison between Néel temperature (T_N) for bulk and thin film form of $Cr_{100-x}Co_x$ alloy with different values of x. From Table 1 it is seen that the T_N for Cr-Co system in epitaxial thin film form is shifted towards the lower temperature than its corresponding value in bulk form. The shift in triple point concentration (x_L), triple point temperature (T_L) and the decrease in T_N in epitaxial thin film form compared to bulk form may be attributed to the dimensionality effects and epitaxial nature of the thin films [7] and need to be investigated further.

The initial decrease in T_N up to x = 2.6 in Figure. 3 can be attributed to the contribution due to interaction between the local moments in Co and the Cr SDW [2]. The pairing effect arising from the antiferromagnetic alignment of the impurity spins parallel to SDW polarization and the depairing effect due to spin and potential scattering acts in opposition to each other. Thus, these two effects give opposite temperature dependence of T_N. Thus, under certain conditions the combined effect may give rise to a decrease in T_N [2, 4].

In high-quality thin films, SDW is quantized [18]. It indicates that change in quantization value influence the carrier density in discrete manner. The changes in charge density takes place when the carriers participate in the formation of SDW. During SDW formation, these carriers become localized resulting in the loss of mobile charge carriers. These effects can be more prominently observed by

Hall coefficient measurements [18]. The reliable profiles of the charge type, carrier density and mobility can also be obtained using Hall coefficient measurements. Thus, it is of interest to study the behaviour of R_H in these Cr-Co alloy thin films. Therefore, it is envisaged that this study will further be extended to include Hall measurements.

4. Conclusions

In the present manuscript the effects of epitaxial growth and dimensionality on the magnetic phase diagram and electrical properties of epitaxial $Cr_{100-x}Co_x$ thin films with $0 < x < 7.2$, prepared on MgO(100) substrates using DC magnetron co-sputtering are reported. XRD analyses confirmed the epitaxial nature of these monolayers. The electrical resistivity measurements on these $Cr_{100-x}Co_x$ thin films revealed that below T_N, the resistivity humps increases with increase in Co concentration giving rise to the dome like anomaly. It is found that the Néel temperature (T_N) for Cr-Co alloy in epitaxial thin film form is lower than the T_N obtained for bulk Cr-Co alloys with similar concentration. The resistivity behaviour of the studied CrCo thin films below T_{min} is found to be complex but appears to be the result of impurity resonant scattering (IRS). The magnetic phase diagram of Cr-Co alloy system in epitaxial thin film form showed shift in triple point concentration to $x_L = 2.6$ at $T_L = 222 \pm 3$ K as compared to bulk Cr-Co alloy system at $x_L = 1.3$ and $T_L = 280$ K. Future work will focus on Hall measurements in order to understand the charge carrier effects.

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