Preparation and characterization of thin ferromagnetic CrO$_2$ films for applications in magnetoelectronics

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Abstract

The theoretically predicted high spin polarization of half-metallic ferromagnets like CrO$_2$ and NiMnSb make them promising materials for magnetoelectronic applications. Highly textured CrO$_2$ films have been prepared by chemical vapor deposition and molecular beam epitaxy. The temperature-dependent magnetotransport data has been correlated with electronic properties of CrO$_2$. Over a wide temperature range (150–330 K) the resistivity follows a $T^2$ behaviour, consistent with electron-electron scattering. Near the Curie temperature of CrO$_2$ no metal-insulator transition, a magnetoresistance of $\sim 7\%$ ($B = 9\, T$) and an enhancement of the resistance due to electron-magnon scattering are observed. © 2000 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Over decades chromium dioxide (CrO$_2$) is a well-known material for magnetic recording tapes. But for novel applications, the most striking feature of CrO$_2$ is the theoretically predicted half-metallic ferromagnetic behavior, which nominally results in 100% spin polarization for spin-up electrons at the Fermi energy $E_F$ [1,2]. The Fermi energy $E_F$ crosses the Cr 3d-spin-up band whereas the spin-down band shows an energy gap $\Delta E$ of 1.5 eV. Spin-polarized photoemission [3] experiments as well as superconducting point contact measurements [4] reveal a spin polarization of over 90%. This unique property makes CrO$_2$ a promising candidate material for magnetoelectronic applications. The performance of magnetoelectronic devices depends strictly on the magnitude of the spin polarization of the ferromagnets used. According to Julliere’s model [5] the magnetoresistance (MR) of magnetic tunnel junction increases with increasing spin polarization of the electrode materials. In this article we discuss structural, magnetic and magnetotransport properties of CrO$_2$ films prepared by chemical vapor deposition (CVD) in comparison with films prepared by oxide molecular beam epitaxy (oxide-MBE).
2. General properties of CrO$_2$

CrO$_2$ crystallizes in the rutile structure with lattice constants of $a = 4.421$ Å and $c = 2.916$ Å [6]. The Cr atom in the center of the unit cell is octahedrally surrounded by oxygen. The CrO$_2$ phase is very susceptible to changes in temperature. Above 400°C under atmospheric pressure CrO$_2$ degrades into Cr$_2$O$_3$ which is an antiferromagnetic insulating phase. CrO$_2$ is one of a few oxides which are metallic and ferromagnetic. The ordering temperature is $T_c = 391$ K. In contrast to doped manganites such as La$_{1-x}$(Ca,Sr)$_x$MnO$_3$ with a mixed valence of the Mn ions (Mn$^{3+}$, Mn$^{4+}$) pure CrO$_2$ with a formal 4+ valence state of the Cr ions shows metallic conductivity and ferromagnetic ordering. Self-consistent spin-polarized band structure calculations describe CrO$_2$ as a so-called half-metallic ferromagnet [1,2,7,8] with a magnetic moment of 2$\mu_B$ per Cr atom [9]. Recently, Korotin et al. [10] interpreted ferromagnetic ordering in CrO$_2$ in terms of a double exchange mechanism [11]. Due to oxygen 2p-states at $E_f$ CrO$_2$ is metallic and not a Mott insulator with two electrons in the $t_{2g}$ orbitals, which would lead to an insulating ground state with antiferromagnetic order. One of the two electrons of Cr$^{4+}$ is $\pi$ bonded with the oxygen 2p-orbitals and forms a partially filled narrow band at the Fermi level. As a consequence one of the two 3d-electrons per Cr atom is localized whereas the other one is itinerant making CrO$_2$ a self-doped double exchange ferromagnet. In the double exchange picture not only charge but also magnetic order is transferred by the itinerant electrons. The spin of these itinerant electrons interacts with the localized chromium-spins and transfers a ferromagnetic order to them. Therefore conduction electrons are more mobile when the localized spins are aligned parallel than without magnetic order, thus pointing towards a concomitant metal–insulator transition.

3. Preparation techniques

Chemical vapour deposition (CVD) and molecular beam epitaxy (MBE) using ozone have been investigated and compared for preparing CrO$_2$ thin films of high crystalline quality.

3.1. CVD CrO$_2$ films

The CVD process has been performed following the procedure suggested by Ishibashi [12]. Decomposing CrO$_3$ powder at 260°C in a reaction-tube furnace under a constant oxygen gas flow of atmospheric pressure leads to a deposition of a CrO$_2$ film on a substrate, which temperature is adjusted to approximately 390°C. For higher substrate temperatures CrO$_2$ decomposes to the thermodynamically more stable Cr$_2$O$_3$. The growth of a 200 nm thick film applying the CVD technique takes several hours. The growth conditions and the texture of CrO$_2$ films have been investigated for Al$_2$O$_3$ (000 1) and (1 0 0) oriented substrates.

3.2. MBE CrO$_2$ films

In case of the MBE growing process pure Cr was thermally evaporated. During deposition an ozone atmosphere close to the substrate oxidized Cr to CrO$_2$. The deposition has been done at various substrate temperatures in an area of 300–450 K. Above 100°C the CrO$_2$ surface degrades to lower oxidized states like Cr$_2$O$_3$. An annealing procedure in an oxygen atmosphere was investigated in order to reduce the surface roughness of the CrO$_2$ films. The main problem is the high resistivity of $10^4$Ω cm due to poor crystalline properties because of restricted substrate temperature area for the CrO$_2$ growth.

4. Structural and magnetic properties

For potential applications in magnetoelectronics it is essential to examine and optimize both crystalline and magnetic properties as well as magneto-transport properties. Especially for tunnel junction applications roughness and homogeneity of the electrodes are critical for high-performance devices.

4.1. MBE CrO$_2$ films

X-ray diffraction and TEM imaging performed on CrO$_2$ films deposited by MBE technique
indicate a microcrystalline growth of CrO$_2$ with a texture depending on the substrates (Al$_2$O$_3$(0001), TiO$_2$(100)) used. The average CrO$_2$ crystallite size is in the range of 10 nm. An annealing procedure under oxygen atmosphere did not increase the crystallites size, whereas the surface roughness measured by STM (scanning tunneling microscopy) decreased from 100 to 15 Å by heating the substrate during deposition. We found a 1/T-dependence for the surface roughness applying these substrate temperatures.

4.2. CVD CrO$_2$ films

The X-ray diffraction pattern (Fig. 1) of CrO$_2$ films prepared by the CVD process shows dominant CrO$_2$ (200) and (400) peaks indicating an a-axis growth. Peaks with small intensity due to misoriented CrO$_2$ and impurities (mainly Cr$_2$O$_3$) have been observed. Films deposited on Al$_2$O$_3$ (1 0 1 0) substrates exhibit a preferred c-axis orientation. However, the diffraction peaks are less intense and broader than for films deposited on Al$_2$O$_3$ (0001) substrates. On the basis of (0001) oriented films the a-axis length was determined to 4.44 Å which is in very good agreement with the published value [6].

The magnetic properties were investigated by SQUID magnetometry. These measurements show a clear ferromagnetic hysteresis and also support the assumption of a colinear relation of the crystallographic c-axis and the magnetic easy axis. This result confirms previous measurements on CrO$_2$ single crystals [13], whereas measurements on polycrystalline samples seem to show an angle of 30–40° between the easy magnetic axis and the c-axis [14,15]. Films grown on Al$_2$O$_3$ (0001) substrates show a remanent magnetization parallel to the c-axis of $M_r = 2.9 \times 10^{-3}$ emu, which gives a magnetic moment approximately $2\mu_B$ per Cr-atom.

Characterizing surface properties, especially specifying the surface roughness, AFM linescans have been performed which give a rms roughness of 4–8 nm for 200 nm thick CVD-films. TEM images of films grown on Al$_2$O$_3$ (0001) substrates were taken to better understand the growth mechanism and to characterize the film/substrate interface. As demonstrated in Fig. 2(a) the TEM image shows that the growth starts with a thin (less than 40 nm) Cr$_2$O$_3$ layer. The main reason for this is the excellent lattice match for these two hexagonal lattice structures and, additionally, the starting conditions

![Fig. 1. X-ray diffraction pattern of a CVD CrO$_2$ film deposited on an Al$_2$O$_3$ (0001) substrate. The strong (200) and (400) reflections indicate a-axis texture of the CrO$_2$ film.](image1)

![Fig. 2. (a) TEM (cross section) image of a CrO$_2$ film on Al$_2$O$_3$ (0001). A thin Cr$_2$O$_3$ layer at the film/substrate interface is visible before the onset of columnar growth of CrO$_2$. (b) The strong contrast between two crystallites especially the rippled interfaces is given by the contact of CrO$_2$ and Cr$_2$O$_3$ crystallites (black arrow). The smoother contrast indicates grain boundaries between CrO$_2$ crystallites of different in-plane orientation (white arrow).](image2)
were not well defined regarding the temperature profile along the reaction-tube furnace and the substrate temperature. Assuming a constant growth-rate the thickness of the first $\text{Cr}_2\text{O}_3$ layer coincides with the time until a constant substrate temperature of 390°C was established. After the 40 nm thick $\text{Cr}_2\text{O}_3$ buffer layer a columnar growth of $\text{Cr}_2\text{O}_3$ has started disturbed by some $\text{Cr}_2\text{O}_3$ grains as indicated by a black arrow in Fig. 2(a). The gradual change in contrast within the $\text{Cr}_2\text{O}_3$ layer occurs when two (100) oriented grains of different in-plane orientation are in close contact indicated by a dashed arrow. The identification of the different oxide phases was made by electron diffraction techniques. The top view TEM image (Fig. 2(b)) shows the in-plane misalignment of individual $\text{Cr}_2\text{O}_3$ crystallites. As in the cross-section image the strong contrast and the rippled interfaces between two crystallites are due to grain boundaries between $\text{Cr}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$ (black arrow), whereas the gradual contrast (dashed arrow in Fig. 2(a)) indicates a grain boundary between $\text{Cr}_2\text{O}_3$ crystallites with different in-plane orientation (white arrow).

5. Magnetotransport properties of CVD $\text{CrO}_2$ films

MR measurements were performed in a variable temperature high field cryostat for magnetic fields up to 10 T. The applied field was in the film plane and perpendicular to the current. The resistivity has been determined applying a four-probe lock-in technique.

For a better interpretation of the low-temperature MR data performed on CVD $\text{CrO}_2$ films we prepared polycrystalline $\text{CrO}_2$ samples by sedimentation of $\text{CrO}_2$ powder in alcohol on glass substrates. Fig. 3(a) shows the resistance of such $\text{CrO}_2$ powder samples as function of an external magnetic field and temperature. At 7 K the MR reaches $-26\%$ and can be interpreted in terms of an intergrain tunneling magnetoresistance (ITMR) [16,17]. An exponential decrease of the MR-effect with increasing temperature up to $\pm 80$ K has been measured. This temperature dependence of the MR ratio has been interpreted by the presence of two conduction mechanisms [16,17]. In the low-temperature regime ($< 40$ K) spin-dependent tunneling between adjacent $\text{CrO}_2$ crystallites dominates, whereas for higher temperatures ($> 40$ K) a thermally activated non spin-conserving hopping process of electrons takes over. The dominance of the spin-conserving tunneling mechanism leads to the large MR measured at low temperatures ($< 40$ K). The maximum of resistivity was found at an applied field of $B_c = \pm 80$ mT which coincides with the coercivity of the sample. At the coercive field the magnetic order in the $\text{CrO}_2$ grains is minimized and consequently the spin-dependent scattering is maximal.

Fig. 3. (a) Intergrain tunneling magnetoresistance (ITMR) of a polycrystalline $\text{CrO}_2$ sample. The arrows show the magnetic history of the sample. (b) Exponential decrease of $\Delta R/R$ with temperature.
We also examined the magnetotransport properties of CVD–CrO$_2$ films. Fig. 4(a) shows the resistivity as function of temperature in magnetic fields of 0 and 9 T. Over the whole temperature range the resistivity is smaller in an applied field than for $B = 0$ T, which leads to a negative magnetoresistance. In Fig. 4(b) the magnetoresistance $\Delta R/R = [R(9T) - R(0T)]/R(0T)$ is plotted from 5 K to room temperature. The maximum of magnetoresistance $\Delta R/R = -10.2\%$ occurs at a temperature of 240 K. Below 50 K the MR increases again probably due to the well-known intergrain tunneling effect [17] which is limited to the low-temperature range. The origin of the minima (labeled by arrows) at 200 and 280 K of $\Delta R/R = -6.4\%$ is still unknown; they were also reported by Suzuki et al. [18]. In the temperature range of 150–330 K we found a metallic $T^2$ behaviour of the resistance. This $T^2$-dependence is an indication for a dominating electron–electron scattering mechanism in this temperature range. At higher temperatures a deviation of the $T^2$-dependence of the resistance indicates that an additional scattering mechanism contributes to the total resistivity (see Fig. 5). Electron–magnon scattering with a $T^{4.5}$-dependence probably contributes to the resistance in the vicinity of $T_c$. For lower temperatures electron–magnon-scattering is suppressed due to the semiconducting behaviour of the minority spin channel.

Fig. 4. (a) Resistivity as function of temperature of a CVD–CrO$_2$ film at $B = 0$ T and $B = 9$ T. (b) Temperature dependence of the MR.

Fig. 5. $T^2$-dependence of the resistivity of CrO$_2$. 
6. Conclusion

The preparation process of CrO$_2$ films via chemical vapor deposition (CVD) and oxide molecular beam epitaxy (oxide MBE) has been compared. In general, the CVD process leads to CrO$_2$ films of higher crystalline quality and lower resistivity. Using highly textured CVD CrO$_2$ films the transport and magnetotransport characteristics have been interpreted by means of electronic properties of half-metallic CrO$_2$. The temperature dependence of the resistivity is consistent with electron-electron (150–330 K) and electron-magnon scattering close to the ordering temperature. Further research is in progress correlating electronic properties of CrO$_2$ with magnetotransport data.

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References