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Molecular beam epitaxial growth of Cr/Fe, Ag/Fe, Ag/Cr and Ag/Co superlattices on MgO (001) substrates

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Cr/Fe and Ag/Cr, Fe, Co superlattices (SLs) have been grown by molecular beam epitaxy on MgO (001) substrates. The results are compared with those previously obtained on GaAs (001), on the basis of reflection high-energy electron diffraction, sputter-depth Auger profile and X-ray diffraction experiments. It is shown that MgO substrates, which are easier to prepare than GaAs prior to epitaxial growth, allow the growth of high quality metallic SLs.

1. Introduction

During the last few years, molecular beam epitaxy (MBE) has facilitated the growth of high quality magnetic multilayer structures. Among them, sandwiches or superlattices (SLs) of Ag/Fe and Cr/Fe have exhibited new and exciting properties, including perpendicular magnetization for Ag/Fe sandwiches and SLs [1–3] and antiferromagnetic coupling and giant magnetoresistance effects for Cr/Fe SLs [4]. Up to now, the MBE growth of SLs in these material systems has been mainly performed on GaAs (001) substrates. The successful use of such substrates necessitates the growth of a buffer layer in order to obtain a smooth and well ordered surface suitable for the subsequent growth of the metallic SLs. This requirement obviously complicates the growth process. Moreover, when a GaAs buffer layer is grown, residual arsenic molecules resulting from the GaAs growth may affect the overall SL properties by reacting with Fe layers. We report here on the use of MgO (001) as an alternative substrate for the growth of high quality Ag/Fe and Cr/Fe SLs. The results show that the overall properties of SLs grown on MgO and GaAs substrates are similar. Moreover, it is shown that MgO (001) substrates can also be used to grow high quality Ag/Cr and Ag/Co SLs.

2. Experimental detail

The growth experiments have been performed in an MBE system designed in our laboratory and equipped with high-temperature effusion cells

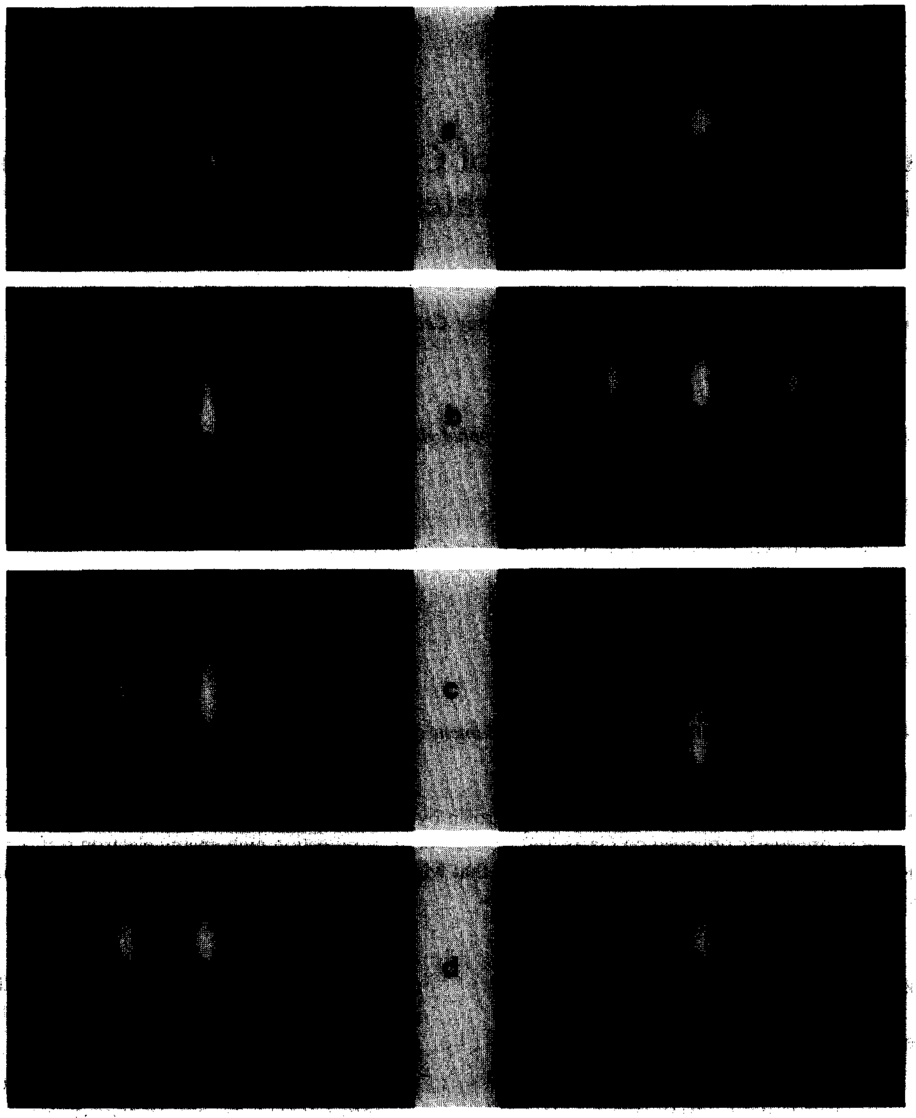

Fig. 1. Characteristic RHEED patterns of (a) MgO substrate after heating at 450 °C for 15 min (left, ⟨100⟩ azimuth; right, ⟨110⟩ azimuth); (b) 20th period of a (Ag 60 Å/Fe 7 Å)$_{20}$ Sl (left, Ag, right, Fe); (c) 30th period of a (Ag 30 Å/Cr 5 Å)$_{34}$ SL (left Ag, right Cr);(d) 2nd period of a (Cr 12 Å/Fe Å)$_{30}$ SL (left Cr, right Fe).

heated by electron bombardment. Additional details can be found elsewhere [5]. Prior to epitaxial growth, the GaAs substrates were simply deoxidized by dipping into a HCl/methanol solution [6]. By heating in the 450–550 °C temperature range under a suitable As_4 partial pressure, it is then possible to induce a standard 2 × 4 reconstruction surface. However, at this stage the surface is still rough and the growth of a GaAs buffer layer is required in order to obtain high-quality epitaxial metallic multilayers [7–9]. Before the subsequent growth of metallic SLs, the residual arsenic pressure, resulting from the GaAs growth should be decreased down to the 10^{-10} Torr range. The growth process on MgO substrates is simpler. MgO substrates (from Sumitomo) are simply heated in the MBE chamber around 450 °C for 15 min, without preliminary chemical etching. A 1 × 1 reflection high-energy electron diffraction (RHEED) pattern exhibiting strong Kikuchi features, and characteristic of a smooth surface, is then obtained (fig. 1a). However, it should be noted that RHEED observations on the bare substrate are more difficult than for GaAs due to strong charging effects, which are difficult to eliminate.

On both GaAs and MgO substrates, metallic SLs are grown using a relatively low growth rate of 500 Å/h for all the elements, and a low growth temperature (30–60 °C). Growth was continuously monitored using RHEED. Since the growth chamber is connected under vacuum with a scanning Auger system, surface analysis could be performed at the different stages of the growth, and ion-beam sputter depth profiles of the grown structures could also be easily performed. Finally, the structural properties of SLs are controlled by standard X-ray diffraction techniques.

3. Results and discussion

3.1. Ag / Fe, Ag / Cr and Cr / Fe superlattices

One of the main differences between the growth on MgO (NaCl structure, $a = 4.20$ Å) and GaAs (zinc-blende, $a = 5.65$ Å) substrates is the occurrence of different epitaxial relationships for the metals involved in the superlattices. In particular, while the (112) orientation is found when Cr is grown on GaAs (001) [7], it is the (001) orientation which occurs on MgO (001). On the other hand, the growth of Ag on MgO gives rise only to the (001) orientation, eliminating the problem encountered in the case of GaAs susbtrates, for which both Ag (011) and (001) orientations can be present at the same time [8,9]. However, a better Ag (001) single-crystal film is obtained when a thin nucleation layer (10–20 Å) of Fe (001) or Cr (001) is first deposited on MgO (001). As previously reported [8,10,11], such a nucleation layer is a strict prerequisite for the growth of high quality Ag/Fe SLs on GaAs (001). However, in that case Cr, which is oriented (112), does not allow the growth of a good single-crystal Ag layer. Another difference between the two substrates is that, while a clearly defined (6 × 6) reconstruction is observed when Ag is grown (via a Fe nucleation layer) on GaAs, a 1 × 1 unit cell is always obtained for the growth on MgO (via a Fe or Cr nucleation layer).

The epitaxial relationships observed when using MgO substrates are summarized as follows:

$$\mathrm{Fe_{bcc}},\ \mathrm{Cr_{bcc}}\{001\}\langle 110\rangle \parallel \mathrm{Ag_{fcc}},$$

$$\mathrm{MgO_{NaCl}}\{001\}\langle 100\rangle$$

with $a_{Fe} = 2.86$ Å, $a_{Cr} = 2.88$ Å, $a_{Ag}/\sqrt{2} = 2.89$ Å and $a_{MgO}/\sqrt{2} = 2.97$ Å.

In the case of GaAs substrates, epitaxial relationships have been previously reported [5,7–9].

Apart from these differences, the overall structural characteristics of Ag/Fe, Ag/Cr and Cr/Fe superlattices are almost identical. Since results obtained using GaAs substrates have been previously reported [5,7–9], we focus here on structural features associated with the growth on MgO substrates.

Typical examples of RHEED patterns recorded during the growth of Ag/Fe, Ag/Cr and Cr/Fe SLs are given in fig. 1. As in the case of GaAs substrates, the RHEED patterns observed for the Ag/Fe (fig. 1b) and Ag/Cr (fig. 1c) couples are indicative of a rather smooth growth front. The transition between the characteristic patterns corresponding to Ag and Fe or Cr layers is rapid, within one or two monolayers, indicating the formation of sharp interfaces. Also, in analogy with the behaviour observed on GaAs substrate, Fe or Cr layers are always slightly rougher than the Ag ones. Therefore the interfaces are not strictly symmetrical; for each period, Ag (lower surface energy) smoothens the Fe or Cr layer surface. Presumably because of this smoothing effect, there is no noticeable degradation of the RHEED patterns even after the deposition of several thousand ångström thick SLs. On the contrary, even if the first grown Cr/Fe SL periods exhibit RHEED patterns characteristic of sharp interfaces and good single-crystal growth (fig. 1d), a slight but continuous degradation occurs as the growth proceeds further. Such degradation is observed for both GaAs and MgO substrates. This similarity is found despite the fact that there is compressive strain for Fe and Cr epitaxially deposited on GaAs (001)

($\Delta a/a = +1.4\%$ and $+2.0\%$ respectively), while severe tensile strain results from the growth on MgO (001) ($\Delta a/a = -3.5\%$ and -3% respectively). With the aim of decreasing the epitaxial strain energy, we have used thick Ag buffer layers ($\Delta a/a = -0.7\%$ and -0.1% for Fe/Ag and Cr/Ag respectively) or even quasi-lattice matched $In_{0.28}Ga_{0.72}As$ buffer layers [9]. No significant improvement was found. It can therefore be concluded that substrate-induced strain is not the driving force behind the observed disordering when increasing the thickness of Cr/Fe superlattices.

In order to confirm that there is no significant intermixing between individual layers of the SLs or between MgO substrates and SLs, ion beam (Ar^+, 1 keV) sputter-depth Auger profiles have been performed. Auger electron signal intensities were deduced from dN/dE peak-to-peak heights measured using kinetic energy windows centered on the most intense line of Ag (336–361 eV), O (495–520 eV), Cr (520–538 eV), Fe (688–708 eV), and Mg (1171–1191 eV). The results corresponding to 4 periods SLs of Ag(60 Å)/Fe(30 Å), Ag (60 Å)/Cr(30 Å) and Cr(45 Å)/Fe(45 Å) are presented in figs. 2a, 2b and 2c, respectively. Although Auger measurements are more difficult for SLs grown on MgO substrates than for those grown on GaAs substrates due to charging effects, the measured profiles are similar. The contributions of each individual layer are clearly resolved even in the case of Cr/Fe superlattice (fig. 2c). Moreover, intermixing between the MgO substrate and the SL layers, if present, is limited to the first deposited SL layer, and is probably less than 15 Å in thickness, which is the estimated depth resolution in the present experiments.

Finally, X-ray diffraction was performed in order to determine the overall structural properties, and in particular the periodic ordering of the superlattices. Diffraction measurements were performed in the $\theta/2\theta$ geometry using Cu Kα radiation monochromatized after the sample by a pyrolitic graphite ((002) reflection) which also eliminates the Fe fluorescence. Spectra corresponding to (Ag 60 Å/Fe 7 Å) × 15, (Ag 30 Å/Cr 30 Å) × 34 and (Cr 12 Å/Fe 20 Å) × 30 superlattices grown on MgO are presented in figs. 3a,

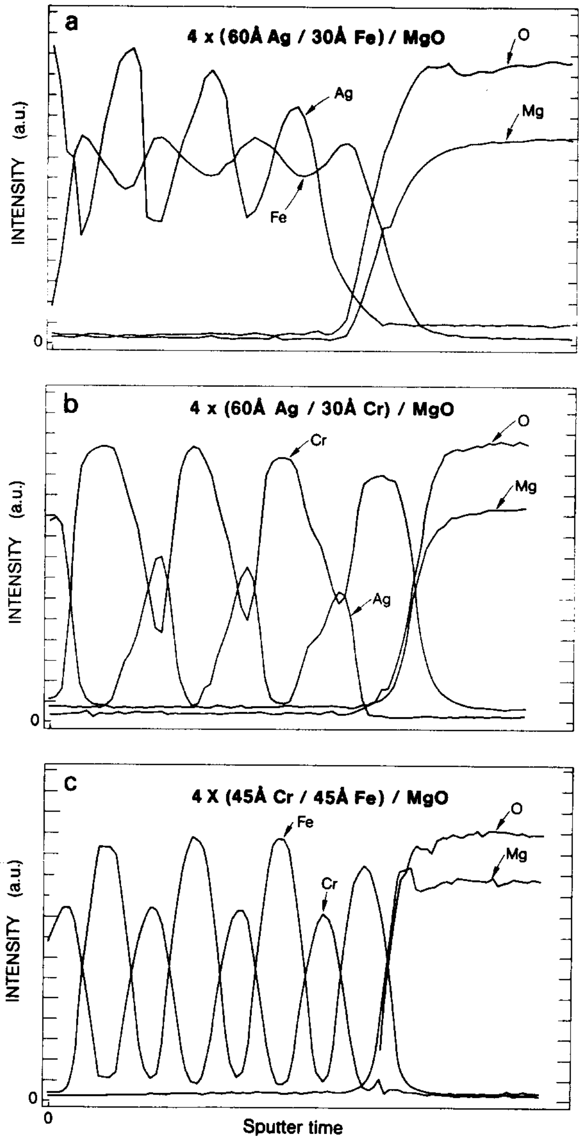

Fig. 2. Ion beam sputter depth Auger profiles of four period SLs grown on MgO (001): (a) Ag(60 Å)/Fe(30 Å); (b) Ag(60 Å)/Cr(30 Å); (c) Cr(45 Å)/Fe(45 Å).

3b and 3c, respectively. The spectra are similar to those obtained for SLs grown on GaAs [9]. In particular several satellites are identified for both Ag/Fe and Ag/Cr SLs between Ag and Fe (or Cr) Bragg peaks. These satellites indicate that well-ordered SL structures with sharp interfaces are achieved for Ag/Fe and Ag/Cr. Simulations

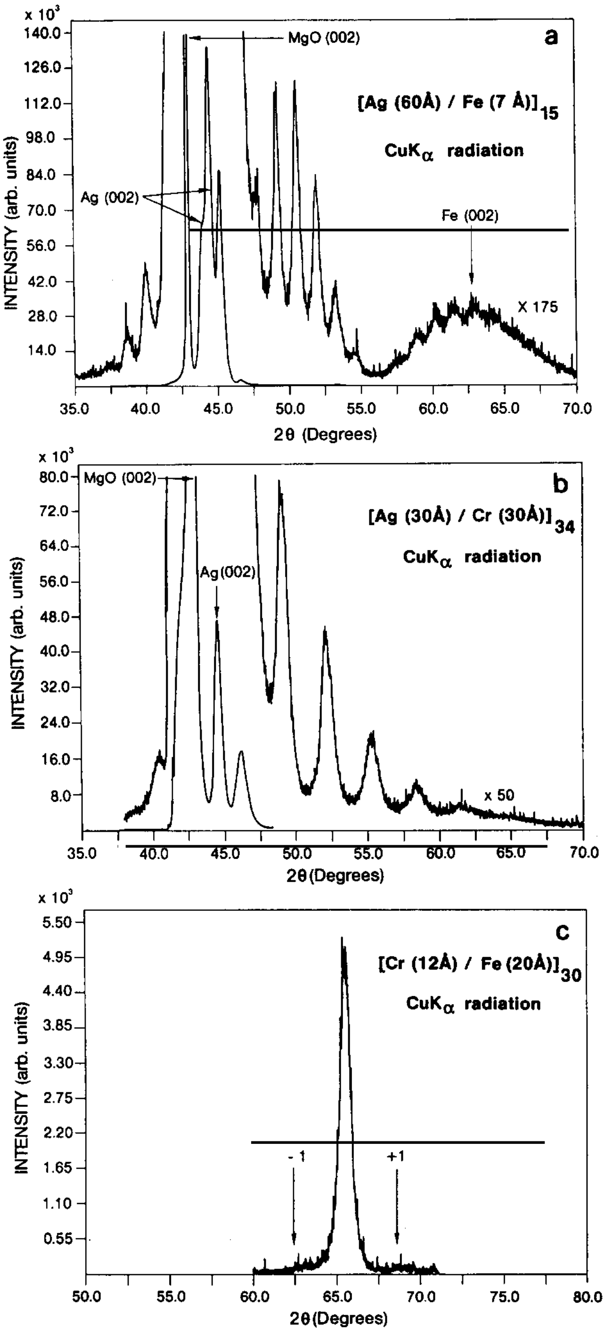

Fig. 3. X-ray $\theta/2\theta$ diffraction patterns around the first Bragg peaks for different SLs grown on MgO (001). Note that we observe in spectrum (a) two Ag (002) peaks, due to buffer and SL layers, respectively.

are in progress to estimate the influence of the two interfaces (Ag/Fe and Fe/Ag or Ag/Cr and Cr/Ag) on the satellite intensities, and to determine if they give rise to the asymmetry in the number of satellites observed around the (002) Bragg peaks. On the other hand, we only detected two weak satellites on each side of the (002) Cr/Fe SL reflection, despite the fact that there is no substrate peak obscuring their observation. One of the origins of these weak intensities is the absorption of X rays by Fe. We plan to carry out further experiments near the K-absorption edge of Cr in order to enhance the peak satellite intensity as in Fe/Mn SLs [12] and to better understand the nature of the interfaces for this system.

Concerning the magnetic properties of SLs grown on MgO (001), it should be noted that up to now no perpendicular magnetization has been found in Ag/Fe SLs grown on MgO (001), although such behavior has been observed in identical structures grown on GaAs (001) [3]. This difference may be related to the fact that for Ag layers grown on MgO no surface reconstruction occurs, while when grown on GaAs a clear (6 × 6) reconstruction is observed. Also, no RHEED oscillations are observed during the growth of Ag on MgO in contrast with the behavior found on GaAs [8]. It seems therefore that Ag layers are of lower quality when grown on MgO, although X-ray diffraction results on Ag/Fe SLs grown on MgO and GaAs substrates are comparable. The difficulty of obtaining perpendicular magnetization in the case of MgO substrates indicates that it is probably very sensitive to the atomic-scale perfection of the interface between Ag and Fe layers.

3.2. Ag/Co superlattices

Co-based multilayer structures have recently attracted considerable attention [13–18] because of their magnetic properties, such as perpendicular magnetic anisotropy, potentially of interest for high-density magnetic recording. Moreover, epitaxial strain in such systems may impose the formation of Co metastable phases, giving rise to new magnetic properties. Depending on the substrate structure and/or superlattice structural parameters (individual layer thickness, nature of the alternating metals), the Co layers crystallize in the usual hcp or in fcc [17,21–23] and bcc [2,19–21] metastable phases.

Among the different metals which can be alternated with Co to give single-crystal SLs, Ag has been studied less than other noble metals such as Au [14,15], Pt [13], Pd [13] or Cu [16]. However, very recent results indicate that the Ag/Co couple is a good candidate to obtain enhanced magnetoresistance effects [23,24].

When Co is directly deposited on MgO (001) substrates at room-temperature, it crystalizes in the (001) hcp orientation. However, if Ag is intercalated between MgO and the Co layer, it is the fcc phase which occurs with the following epitaxial relationship:

$$Co_{fcc}\{001\}\langle 100\rangle \| Ag_{fcc}\{001\}\langle 100\rangle .$$

After a nucleation layer of 20 Å, of Cr on MgO, a thin Ag layer (~ 60 Å) is in fact sufficient to impose the fcc phase of Co. The RHEED pattern of this phase is observed up to 400 Å, the thickest Co layer deposited in the present work. However, nuclear magnetic resonance (NMR) experiments [25], although confirming the presence of the metastable fcc phase, indicate also a contribution of the hcp phase.

Different superlattice structures have been grown at room-temperature with individual layers ranging from 30 to 60 Å for Ag and 5 to 60 Å for Co. Although the RHEED pattern associated with the fcc Co phase is always observed for a 30 period SL of Ag(30 Å)/Co(5 Å), change in the RHEED pattern occurs with increasing Co layer thickness. It is tentatively associated to the phase transition from fcc to hcp. For a superlattice consisting of alternating layers of 60 Å Ag and 10 Å, 20 Å or 60 Å Co, the transition appears after ~ 15, 3 and 1 periods of growth, respectively. This result is in contrast to the fact that for a single layer of Co on Ag (001) the fcc phase is still present after several hundred angstroms deposition. It is clearly more difficult to preserve the fcc phase when alternating growth of Ag and Co is performed. This is probably due to the fact that the structural quality of the Ag layers grown on top of the Co layers degrades as a function of individual and integrated thicknesses of the Co layers, as deduced from the RHEED pattern evolution. Indeed the RHEED pattern of the fcc Co phase disappears when the Ag layer assumes

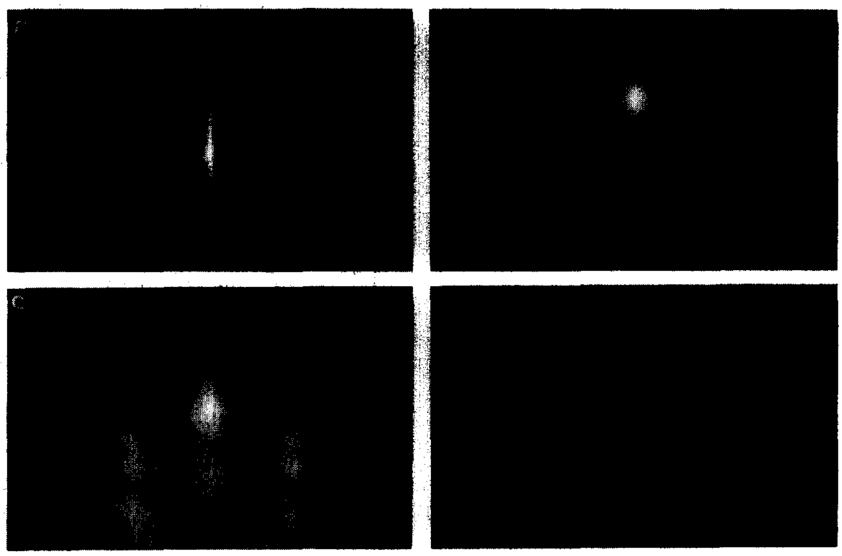

Fig. 4. Characteristic RHEED patterns of a (Ag 60 Å/Co 20 Å)$_{18}$ SL: (a) first Ag layer ((001) single orientation); (b) first Co layer (fcc phase); (c) last Ag layer (non-single orientation); (d) last Co layer (hcp phase).

several orientations. Another remarkable point is that when Co is grown on Ag (001), it assumes its bulk lattice parameter (3.54 Å) from the very first monolayers deposited. In other words, there is no pseudomorphic growth in this system.

Typical RHEED patterns taken during the growth of a (Ag 60 Å/Co 20 Å) $\times$ 18 are presented in figs. 4a–4d. Figs. 4a and 4b correspond respectively to Ag and Co layers in the first SL period while figs. 4c and 4d correspond to Ag and Co layers in the last SL period, i.e. at a stage where the Ag layer is no longer of a single orientation and the Co layer is mainly in the hcp phase. From the point of view of transport properties, Ag/Co SLs epitaxially grown on MgO (001) appear to be promising structures. The magnetoresistance ratio attains 20% at 4.2 K with magnetoresistance peaks at $\pm$200 Oe [26].

4. Conclusion

It is shown that a MgO (001) substrate can be used instead of GaAs (001) for the MBE growth of high quality Cr/Fe, Ag/Fe, Ag/Cr, and Ag/Co epitaxial superlattices.

The structural properties of these superlattices grown on both substrates are similar. The main difference resides in the epitaxial relationships between the metals and the substrates. In particular, Cr and Ag take the (001) orientation on MgO (001) while on GaAs (001) the observed orientations are (112) for Cr and (110) and/or (001) for Ag. Another difference is that for Ag layers grown on MgO no surface reconstruction occurs, while when grown on GaAs a clear (6 $\times$ 6) reconstruction is observed. This difference may be related to the fact that no perpendicular magnetization has been found, at least up to now, for Ag/Fe SLs grown on MgO, contrary to the case of identical SLs on GaAs (001).

On the other hand, in the present early state of our investigations, it seems easier to grow Ag/Co superlattices on MgO than on GaAs. It is found that thin layers of Co epitaxially grown on Ag (001) are mainly in the fcc metastable phase, the transition towards the hcp phase being rapidly observed in SL structures when increasing the Co thickness. These superlattices have already exhibited promising transport properties such as enhanced magnetoresistance effect.

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