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A Mössbauer study of Co cluster nucleation in Ag

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Abstract. In the present study we aim to investigate the onset of Co cluster formation in Ag by Mössbauer spectroscopy. Hyperfine interaction techniques are very powerful in determining the onset of formation of very small clusters because they probe the atomic environment present at the radioactive probe atom’s site. We employed different sample preparation techniques and discuss the differences between them. We could establish the proper conditions for obtaining a large fraction of Co dimers. The behaviour of the different components in the Mössbauer spectra as a function of the Co concentration allows us to estimate the typical trapping radius for Co dimer formation.

1. Introduction

Magnetic clusters are the subject of many research projects these days, because of their interesting magnetic and thermodynamic properties. Since the discovery of the giant magnetoresistance (GMR) effect in non-magnetic materials loaded with magnetic clusters [1, 2], these systems have become, together with multilayers of alternating magnetic and non-magnetic elements, candidates for a wide variety of technological applications in all fields dealing with magnetic recording.

There are three methods which are commonly applied for obtaining clusters of a magnetic element (Co) in a non-magnetic matrix (Ag). The first one is co-evaporation of the two elements, for instance with a MBE system, the second one is ion implantation of Co into Ag and the third one is deposition by co-sputtering. We used the first and second method for preparing samples in the present study. After the preparative step, Co clusters are readily formed upon annealing the samples, because of the extremely low solubility of Co in Ag, although some initial cluster formation already takes place during the co-deposition process [3] and during the ion implantation. In the latter case the radiation damage in the collision cascade leads to radiation enhanced diffusion, which can speed up the precipitation process.

Very little is known, however, about the initial stages in the cluster formation. One of the purposes of this study is to investigate the influence of the preparation technique on the first stage of the cluster formation process.

For the samples with Co concentrations below 1 at%, we expect, based on the work of Sawicka [4], that almost all Co atoms will be present as monomers or dimers.

Mössbauer spectroscopy on $^{57}\text{Co} \rightarrow ^{57}\text{Fe}$ is a powerful tool in determining the different Co sites, since they appear as distinct components in the Mössbauer spectra. It is noteworthy that the average Co cluster size in the as-prepared state of our samples, especially in the lower Co concentration region, is below the resolution limit of other characterization techniques used in the study of clusters, in particular transmission electron microscopy.

2. Experimental

We prepared three series of samples: series B consists of a MBE-grown Ag layer on a MgO(100) substrate. A Cr buffer layer between MgO and Ag was used to improve the monocrystallinity of the Ag layer. The thickness of the Ag layer is 1200 Å. These Ag layers are monocrystalline in the growth direction and have a columnar structure. The mean diameter of these columns was determined by atomic force microscopy to be $0.1\,\mu\text{m}$. Subsequently $5 \times 10^{13} \text{cm}^{-2}$ mass $^{57}\text{Co}$ ions, about half of which are $^{57}\text{Co}$, were implanted at an energy of 50 keV into the Ag layer. The thickness of the Ag layer is 1200 Å. These Ag layers are monocrystalline in the growth direction and have a columnar structure. The mean diameter of these columns was determined by atomic force microscopy to be $0.1\,\mu\text{m}$. Subsequently $5 \times 10^{13} \text{cm}^{-2}$ mass $^{57}\text{Co}$ ions, about half of which are $^{57}\text{Co}$, were implanted at an energy of 50 keV into the Ag layer. The thickness of the Ag layer is 1200 Å.

Mössbauer spectroscopy was recorded at $^{57}\text{Co}$ and $^{57}\text{Fe}$ is a powerful tool in determining the different Co sites, since they appear as distinct components in the Mössbauer spectra. It is noteworthy that the average Co cluster size in the as-prepared state of our samples, especially in the lower Co concentration region, is below the resolution limit of other characterization techniques used in the study of clusters, in particular transmission electron microscopy.

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Table 1. Doses and energies of $^{59}$Co ion implantations.

<table>
<thead>
<tr>
<th>Series A</th>
<th>Series B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co concentration (at%)</td>
<td>Energy (keV)</td>
</tr>
<tr>
<td>0.05</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>90</td>
</tr>
<tr>
<td>0.15</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>55</td>
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<tr>
<td></td>
<td>90</td>
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<td>0.5</td>
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<td>1.2</td>
<td>16</td>
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<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>90</td>
</tr>
</tbody>
</table>

homogeneous and completely overlapping the $^{57}$Co depth region. The calculation of energies and doses is based on the TRIM code, thereby taking into account the receding of the surface due to sputtering. The implantation parameters are listed in table 1.

Series C consists of three samples with different Co concentrations. Co and Ag were co-evaporated at RT in a MBE system on a MgO(100) substrate with a Fe buffer layer. Afterwards, we implanted $^{57}$Co into these samples. To protect the samples against internal oxidation, which easily occurs at impurities in Ag, a Si passivation layer was evaporated onto the top of the samples. The Co concentration and the crystal quality of the Ag layer were determined by Rutherford backscattering spectroscopy (RBS). The Ag minimum yield increases with the Co concentration as shown in figure 1, indicating that the incorporation of an increasing concentration of the insoluble Co impurity deteriorates the monocrystallinity of the Ag. The respective Co concentrations for these three samples are 3.5, 7.5 and 13 at%. We also prepared, in exactly the same conditions, a fourth sample containing 22 at% Co which we did not, however, measure at RT. It is worth mentioning that Co concentrations above approximately 10 at% can no longer be attained by means of ion implantation because a regime is met at high dose ion implantation in which an equilibrium is reached between an increase in the Co concentration by direct implantation and a decrease by sputtering.

Series A consists of four polycrystalline Ag foils pre-implanted with $^{57}$Co and post-implanted with $^{59}$Co in a way similar to that for series B. The grain diameter of these Ag foils was determined by optical microscopy and is typically 7.5 μm. The purity of the foils is 99.99%. The Co concentrations are 0.05, 0.15, 0.5 and 1.2 at% respectively. The implantation parameters can be found in table 1. All ion implantations mentioned so far were performed at RT.

Figure 1. The Ag minimum yield in RBS spectra as a function of the Co concentration.

3. Results and discussion

The Mössbauer spectra from series A, B and C were recorded in transmission mode at RT and fitted by a least-squares fitting routine. A typical spectrum from each series is shown in figure 2. All spectra from one series were fitted consistently with one single line and two quadrupole-split doublets. A third doublet was added for series A because of the occurrence of internal oxidation. The Mössbauer parameters are listed in table 2. The assignment of the different spectral components is convincingly supported by the overall feature of concentration-dependence, as shown in figure 3. The same sites are populated in all the samples, independent of the preparation technique.

The single line originates from $^{57}$Fe at substitutional sites in the Ag lattice. The linewidth was determined from the spectrum with the largest single line contribution and kept constant at 0.38 mm s$^{-1}$ for all series. Its isomer shift is close to the reference value for $^{57}$Fe in Ag [4] and to the value which we measured for the lowest Co concentration in Ag. The intensity of the single line is more or less independent of the Co concentration for series B. All
Table 2. Consistent Mössbauer parameters of the components present in the spectra from series A, B and C as obtained by least-squares fitting of the spectra. $\delta$ stands for the isomer shift and $\Delta$ for the quadrupole splitting. Isomer shifts are relative to $\alpha$-Fe. We performed source experiments.

<table>
<thead>
<tr>
<th>Series</th>
<th>$\delta_{Q1}$ (mm s$^{-1}$)</th>
<th>$\delta_{Q2}$ (mm s$^{-1}$)</th>
<th>$\delta_{Q3}$ (mm s$^{-1}$)</th>
<th>$\delta_{SL}$ (mm s$^{-1}$)</th>
<th>$\Delta_{Q1}$ (mm s$^{-1}$)</th>
<th>$\Delta_{Q2}$ (mm s$^{-1}$)</th>
<th>$\Delta_{Q3}$ (mm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-0.41(2)</td>
<td>-0.21(4)</td>
<td>-1.00(3)</td>
<td>-0.48(2)</td>
<td>0.43(2)</td>
<td>0.80(4)</td>
<td>2.38(3)</td>
</tr>
<tr>
<td>B</td>
<td>-0.49(2)</td>
<td>-0.21(2)</td>
<td>-0.45</td>
<td>0.74(2)</td>
<td>0.79(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-0.73(2)</td>
<td>-0.22(2)</td>
<td>-0.52(3)</td>
<td>0.67(2)</td>
<td>0.48(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. Mössbauer spectra and least-squares fits from $^{57}$Co in three typical samples versus a SFC absorber.

intensities are shown in figure 3, in which the full symbols represent series A, the open ones series B and the crossed ones series C. At the very low concentration of 0.05 at% in series A, the majority of Co atoms are at substitutional sites. With increasing Co concentration the substitutional fraction is reduced to the value that is found in series B (around 15%). The jump from 59.7 to 13.6% in going from 0.05 to 0.15 at% Co can be understood in terms of the trapping volume of Co for an extra Co atom which we deduced here is considerably larger. This could indicate a Co–Co bond that is stronger than the Co–Al one, which we believe to be caused by the participation of the d electrons in the bonding [7]. On the other hand, part of the magnitude of this large trapping radius may also be apparent and be caused by an enhanced mobility of Co through radiation-enhanced diffusion.

The intensity of doublet 2, which we attribute to small Co clusters, is considerably larger in the sample with 1 at% Co of series B than in the sample with 1.2 at% of series A. We tentatively explain this difference in terms of an enhanced trapping of the Co atoms at grain boundaries [6], the density of which is much higher in MBE-deposited Ag than it is in polycrystalline Ag, as shown by comparison implantation process. From the intensity jump of the single line and assuming, as a first approximation, that the Co atoms are at substitutional Ag lattice sites in the region within which they are homogeneously distributed, one can calculate that the mean distance between two Co atoms is 22.5 Å for 0.15 at% Co and 32.4 Å for 0.05 at% Co. This leads us to the statement that the trapping radius of Co for a second Co atom should lie between those two values. For comparison purposes, we refer to the trapping radii which have been calculated by Verbiest [6] for Co and point defect configurations in Al. The unknown parameters in the model were the trapping volumes, which the authors could determine by fitting their calculated values to experimental data. The trapping radius of Co for an Al interstitial (forming a mixed interstitial ‘dumbbell’) obtained in this way was only 8.3 Å. The trapping radius of Co for Co (probably also forming an interstitial pair) which we deduced here is considerably larger. This could indicate a Co–Co bond that is stronger than the Co–Al one, which we believe to be caused by the participation of the d electrons in the bonding [7]. On the other hand, part of the magnitude of this large trapping radius may also be apparent and be caused by an enhanced mobility of Co through radiation-enhanced diffusion.

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of the typical grain sizes for MBE-deposited layers and polycrystalline foils. This would also explain why the relative intensity of the single line is markedly lower in series B than it is for the sample with 1.2 at% Co from series A.

In the samples from series C only the radioactive $^{57}$Co atoms were introduced afterwards by ion implantation. We expect the metastable sites which are populated by the $^{57}$Co atoms to be relatively more stable than they are for the high-dose ion-implanted samples because there is little radiation-enhanced diffusion during sample preparation. In this way we explain that the substitutional fraction is larger for the co-evaporated sample for comparable Co concentrations (3.5 at% in series C versus 3 at% in series B). Weiß et al. have observed [8] that up to about 5 at% Co was still mostly dissolved within the Ag matrix after a deposition at low substrate temperatures and that precipitation started only at annealing temperatures of 100°C. The decrease in this fraction at higher Co concentrations is a consequence of the onset of dimer and larger cluster formation.

Doublet 3 in series A has an isomer shift (~1.00 mm s$^{-1}$) and a quadrupole splitting (2.38 mm s$^{-1}$) which are typical for the Fe$^{2+}$ state in Fe oxides [9]. Oxygen might have been present in the polycrystalline Ag foils at grain boundaries before the ion implantation and may in addition have been introduced from the sample surface by recoil implantation [10]. This component is not present in series B and C. The very limited intensity increase with Co concentration, together with the observation that the intensity increases during annealing (in an Ar–H$_2$ atmosphere at 150°C) [11], gives support to the idea that oxygen was already present before the ion implantation process and that the oxidation occurs by vacancy-enhanced diffusion.

Doublet 2, the intensity of which increases with Co concentration, is present in all series and can be attributed to $^{57}$Fe in small Co clusters. In the samples of series A, however, the relative contribution from clusters is much smaller than it is for comparable Co concentrations in series B. We believe that this may be caused by oxygen segregation and trapping at some of the dimers and at the smallest clusters’ nuclei. It is indeed known [12], and we confirmed this in a recent cluster annealing study [11], that the presence of oxygen has a strong inhibiting effect on cluster mobility, thus preventing their growth by coalescence. The isomer shift of doublet 2 lies between the literature values for Fe in Co, 0.04 mm s$^{-1}$ [13], and Fe in Ag, indicating that the clusters are sufficiently small to have most of their atoms located very close to, if not at, the interface. We find support for this in the fact that this component in all series is split with a quadrupole interaction strength which is typical for interfaces [14]. Even for the larger Co concentrations in series C no spectral component is present corresponding to $^{57}$Fe located inside Co clusters. We can easily understand this since the Co clusters have formed during the co-evaporation process whereas the $^{57}$Co probes were implanted afterwards and thus did not take part in the cluster formation process. Considering that the diffusion coefficient of Co in Co is still much lower than that of Co in Ag, a $^{57}$Co probe reaching the cluster interface will not populate the inner part. It is worth mentioning that a measurement which we performed at 4.2 K [15] shows that part of this intensity, corresponding to probe sites at the interface of somewhat larger clusters (found in the tail of the size distribution extending into the few nanometres range) exhibits ferromagnetic ordering.

We assign doublet 1 to the contribution from $^{57}$Fe atoms in dimers. Values for Fe–Fe dimers in Ag have been reported by Sawicka et al. [4]. They found a doublet with an isomer shift of 0.38 mm s$^{-1}$ and a quadrupole splitting of 0.8 mm s$^{-1}$ in non-annealed Ag samples implanted with Fe at doses in the range 1.5–3 at%. The dimers which are reflected in the Mössbauer spectra from our samples consist of one Fe and one Co atom. Co–Fe dimers have been investigated by means of matrix isolation experiments by Montano [7]. They appeared in his Mössbauer spectra as a doublet with an isomer shift of 0.55(5) mm s$^{-1}$ (in an absorber experiment) and a quadrupole splitting of 3.60(5) mm s$^{-1}$. We expect that the presence of the Ag matrix around the Co–Fe dimer should reduce the asymmetry of the charge distribution, resulting in a smaller electric field gradient.

From series A it is clear that dimer formation strongly exceeds the value expected from statistical encounters [4] when a critical concentration (lying somewhere within the range 0.05–0.15 at%) is reached, as we explained earlier. The intensity of doublet 1 decreases with increasing Co concentration and is overtaken by doublet 2, clearly reflecting the onset of the Co cluster growth.

4. Conclusions

The influence of the specific sample preparation technique on the first stage in Co cluster formation in Ag is not very pronounced. Only the fraction of Co atoms at substitutional sites depends sensitively on the preparation technique. From the spectral intensities of the different components in the Mössbauer spectra as a function of the Co concentration, we are able to estimate the trapping radius of a Co atom for an extra Co atom to lie in the range 23–32 Å. Part of the $^{57}$Fe is oxidized in the polycrystalline Ag foils. Most of the oxygen was already present in the Ag before the Co ion implantation and the oxidation process is enhanced by vacancy diffusion. We found the proper preparation conditions by which to obtain a large fraction of Co dimers in Ag by the investigation of the dependence of the Mössbauer parameters on the Co concentration, which should allow us to perform future magnetization measurements on Co dimers in addition to the ones on small Co clusters in Ag.

References