Growth and study of Ni nanoparticles films deposited on inert subtrates

S. D'Addato [1,2,*] , L. Gragnaniello[1,2], A. di Bona[1], A. Rota[1], P. Vavassori[1,3], S. Valeri [1,2]

[1] INFM-CNR, S[3] Research Centre, via G. Campi 213/a, 41100 Modena, Italy

[2] Dipartimento di Fisica, Università di Modena e Reggio Emilia, via G. Campi 213/a, 41100 Modena, Italy

[3] Dipartimento di Fisica, Università di Ferrara, Via G. Saragat 1, 44100 Ferrara, Italy.

E-mail:daddato.sergio@unimore.it

Abstract. We report the results of a study on Ni-clusters assembled films deposited on Si(100) and MgO(100) surfaces. The films were produced by deposition of pre-formed Ni nanoparticles generated by a gas aggregation source. The samples topography and growth mode were investigated with SEM, AFM, STM and XPS. MOKE technique was used to determine magnetization curves at T=300 K, T=100 K and T=50K. The films show random paving growth mode, where clusters assemble in agglomerates. From MOKE data we observe a behaviour that can be ascribed to the occurrence of Super Correlated Spin Glass phase at T=300 K, and soft ferromagnetic hysteresis cycles at low temperature, possibly related with a different magnetic phase.

1. Introduction

The interest in metal nanostructured films has grown in the last years because of their fascinating physical properties and their potentiality in various applications, like magnetic recording industry, catalysis and tribology. For example, smaller particles are required in order to realize advanced magnetic memory units [1], but this request constitutes an important challenge, because of the super-paramagnetic limit for the density of recorded bits, which makes conventional recording media with three-dimensional particles unstable. The possibility of depositing preformed gas-phase nanoparticles onto surfaces allows a systematic study of magnetic anisotropy, interparticle exchange interaction, superparamagnetic and ferromagnetic behaviour as a function of particle mass and of film thickness [2]. This investigation is necessary for fundamental and technological reasons, as control of size and shape of nanoparticles is highly desirable, in order to understand their basic magnetic properties and to tailor them to obtain new functional materials. Deposition of gas-phase nanoparticles has been used extensively to produce Fe and Co nanostrucured and granular thin films, giving rise to systems that show a variety of complex magnetic phases depending on particle size, volume fraction and temperature [6-8]. In order to extend this kind of studies to other magnetic materials, we present in this

* To whom any correspondence should be addressed.

paper the first results of an investigation of Ni nanoparticles-assembled films grown on oxidized Si and MgO inert substrates. We chose Si and MgO for their low surface roughness, which make them ideal substrates for our experiments. The deposition has been obtained by making use of a recently developed experimental system, with a gas-aggregation cluster source and a quadrupole mass filter (QMF). We produced films Ni particles of different thickness values, corresponding to regimes where the nanoparticles are dispersed or they constitute a nanostructured film. The samples have been characterized ex-situ with Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Scanning Tunnelling Microscopy (STM). X-ray Photoelectron Spectroscopy (XPS) was used to check morphology and composition. Magneto Optical Kerr Effect (MOKE) experiments have been performed on Ni cluster-assembled films grown on MgO(100) to investigate their magnetic properties at different temperature values.

1. Experimental

Ni cluster-assembled films were prepared in an experimental system consisting of a particle source, a quadrupole mass spectrometer/filter, and a deposition chamber. A beam of nanoparticles is produced with the NC200 cluster source, Oxford Applied Research. The source evaporates metal atoms from a target with magnetron sputtering, and particle aggregation is obtained by means of Ar carrier gas. Different mass distributions can be obtained by changing the gas flow, sputtering power and the length of aggregation region. The mass distribution of the particle beam is analysed with a Quadrupole Mass Spectrometer (QMS), positioned between the source and the deposition chamber. The QMS is used also as a filter, in order to obtain a beam of pre-formed clusters with the desired size, that impinges onto the substrate in the deposition chamber. Ni particles of masses ranging from 7.6×10^4 amu to 3.0×10^6 amu were obtained, corresponding to linear size values between 3 and 10 nm, assuming that the particles have a spherical shape and the same density as bulk Ni. The neutrals particles, which are present in the beam exiting from the source, cannot be filtered with QMF. Their presence has the effect of spreading the size distribution. We minimized this effect with a proper choice of the source parameters, in order to obtain the maximum of the mass distribution corresponding to the desired size. The deposition rate was measured with a quartz thickness monitor (QTM), positioned between the sample and the cluster beam, before and after dosage. The deposition rate depends on the chosen filter resolution. Typical values during our experiments were 0.2 or 0.3 nm/min with a mass resolution $\Delta M/M=0.5$, corresponding to a linear size resolution $\Delta d/d= 0.17$. The base pressure in the deposition chamber was $p=1 \times 10^{-8}$ mbar, raising to $p= 2 \times 10^{-5}$ mbar during the dosage, because of the presence of Ar coming from the gas aggregation area in the NC200 source. The substrates were Si(100) single crystal wafers and MgO(100) single crystal slabs, with surface roughness (defined as root mean square, rms) of 0.04 nm and 0.07 nm, respectively, as measured by AFM. We report film thickness values in equivalent monolayers (ML). We define 1 ML as the quantity of material deposited corresponding to a thickness value equal to the diameter of the particle. For instance, 1 ML of Ni particles of 5 nm diameter corresponds to a quantity of material equal to 5 nm as measured by the QTM. We obtained films of different thickness values, ranging from t=0.1 to t=3 ML. After deposition, the cluster assembled films were removed from the chamber and studied *ex-situ* with SEM, STM, AFM, XPS and MOKE.

1. Results

Figure 1shows a SEM image from Ni nanoparticles deposited on Si(100). The individual particles can be clearly observed. They are randomly distributed, with limited diffusion, in agreement with the random paving growth mode that was already observed for Fe and Co particles deposited on different substrates [2]. A grain analysis gave a lateral size distribution that was fitted with a Gaussian function, giving an average diameter d=9.4 nm, with a width $w=2\sigma= 1.4$ nm, where σ is the Gaussian standard deviation. A similar behaviour was also found for our films grown on MgO(100).

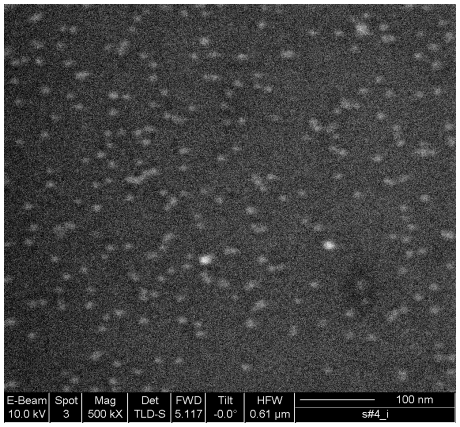

Figure 1. SEM image showing Ni nanoparticles deposited on Si(100).

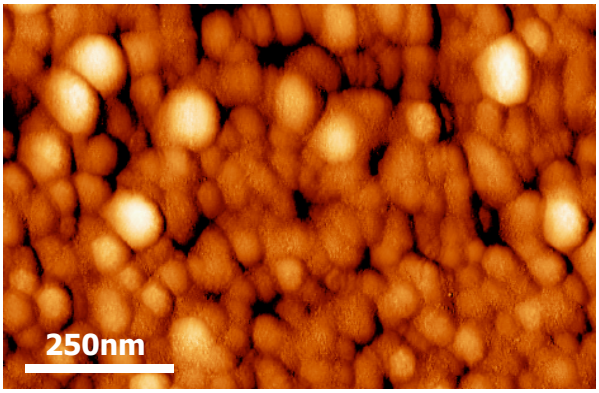

Figure 2. AFM image taken in tapping mode from a Ni assembled cluster film grown on MgO(100). Film thickness t= 1.7 ML, Average linear size of Ni particles d=4 nm

In figure 2 we report an AFM image obtained from a Ni cluster-assembled film grown on MgO (100). The chosen average particle diameter was d=4nm, and the film thickness was t=1.75 ML. The AFM image was obtained in tapping mode. The image shows grains much larger than the individual particles, with an average size of 40 nm, although we a measured a value of rms=4.4 nm, similar to the selected size chosen with mass filtering during the preparation of the sample. The grains are agglomerates of the individual particles, that cannot be directly observed, due to the limited lateral resolution of the microscope. These agglomerates were also observed on Co, Fe and Ti particles films [2]. STM images (not shown here) from a film of Ni particles deposited on Si(100) obtained by our source without using the QMF show that the grains have an internal structure, and individual Ni particles could be singled out. We can conclude that the growth mode and the surface topography of Ni cluster –assembled films present strong analogies with similar systems [2-4]. The Ni particles are deposited in a random paving mode, and they form agglomerates as the film thickness increases.

Since the samples were exposed to air after preparation for *ex-situ* experiments, we performed a XPS analysis in order to determine their level of contamination. Ni2p lineshape anaysis revealed the presence of a mixture of NiO and Ni_2O_3, together with metallic Ni. After a mild Ar^+ sputtering of the sample, the signal coming from oxidized Ni disappeared, revealing that only the particles positioned at the surface were heavily contaminated.

Figure 3 shows MOKE loops from a film of Ni particles with d=4 nm, t=1.75 ML grown on MgO(100), at three different temperature values: T=300 K, T=100 K and T= 50 K. At T=300 K data show no cohercive field H_c. For low temperature values the hysteresis loop opens, H_c increases when passing from T=100 K to T=50 K, and the film reveals soft ferromagnetic behavior. In particular, at T= 50 K we found a value for H_c=40 Oe, and saturation is reached at H=450 Oe. The global anisotropy of the film is in-plane, with no preferential axis along the surface. Data taken at T=300 K could not be fitted with a simple Langevin function. As previously reported, the magnetic configuration of Fe cluster-assembled films at T>50 K is a correlated superspin glass [2,3,5,6]. The Random Anisotropy (RA) model [7] was adopted to explain the magnetic properties of this phase. According to RA, each individual particle has an anisotropy axis randomly oriented, and there is an exchange interaction between the particles. The relative strength between the random anisotropy field and the interparticle exchange field determines the value of a magnetic correlation length, which turns out to be higher that the linear size of the individual particles. In this case, the magnetic vectors tend to

be aligned, but there is a random deviation from perfect alignment producing a smooth rotation of the magnetization within the correlation length [2].

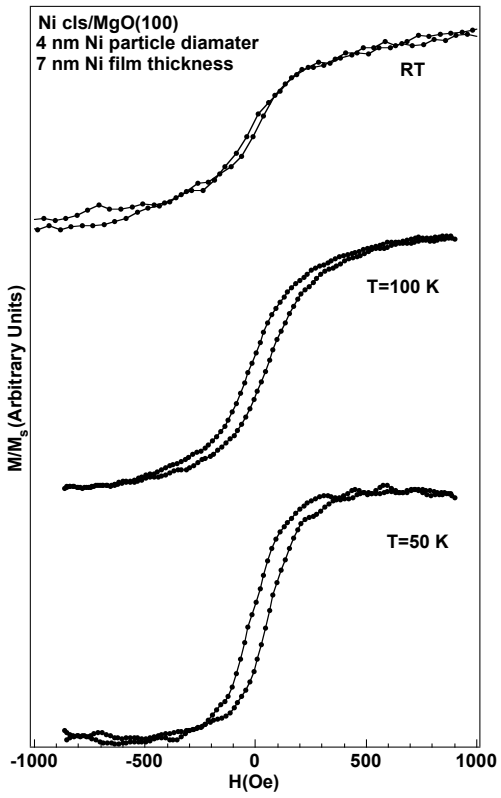

Figure 3. MOKE loops taken from a Ni cluster-assembled film grown on MgO(100) at different temperature values

This model has also been adopted for Ni cluster film grown with a different experimental method [5]. It is reasonable to conclude that the magnetization curves obtained by our MOKE experiment can be interpreted with the same model. The partial oxidation of our film, caused by exposition to atmosphere, can cause the presence of a magnetic dead layer at the surface, and of a thin oxide shell around the single cluster, resulting in an attenuation of the exchange field. At lower temperature, the opening of the hysteresis loop can possibly be attributed to a new magnetic phase [2-5] where collective blocking occurs. In Co assembled cluster films this phase shows spin glass behavior [2]. More work is in progress to understand the evolution of the magnetic properties of the Ni nanoparticles films with temperature and cluster size.

Acknowledgements
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