ORDERED THIN FILMS OF MAGNETIC NANOPARTICLES

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Summary The investigation of physical properties of bulk materials is a traditional approach in materials science. During last decades the interest has been focused on two-dimensional ordered systems of nanometer-size particles with unusual mechanical, electrical, magnetic, optical, chemical properties, which are perspective for applications in electronics, optics, computer science and medicine. In this paper we report on the preparation of well ordered Langmuir-Blodgett films of γ-Fe_2O_3 nanoparticles with an average size of 10nm. Arrangement and homogeneity were confirmed by scanning electron microscopy as well as atomic force microscopy. Magnetic properties were measured by the magneto-optical Kerr effect.

1. INTRODUCTION

The construction of novel nanostructured materials attracts much attention in materials research due to potential applications in electronics, optics and magnetism. Physical properties of materials are in this case determined only by three parameters: the size of particles, their composition and topology of the system. The choice of technology used for organization of the system is thus important from the point of view of macroscopic properties. Preparation and processing of fine magnetic particles is motivated for the last several decades by their variety of applications, such as ferrofluids [1-2], data storage [3-4], and medicine [5-8]. A major basic scientific interest in small magnetic particles has focused on studies of the magnetic properties of single-domain magnetic particle assemblies [9]. More recently, with advances in colloidal nanocrystal synthesis, interest has grown in producing nanostructured magnetic thin films with well-defined structures and controlled properties [10].

In this communication we present the formation of ordered arrays of ferrite nanoparticles by means of the Langmuir-Blodgett technology whose superior property dwells in the capability of depositing a defined number of monolayers (layer-by-layer) at ambient temperature, i.e. even a monomolecular-layer possible and prepare two-dimensional and quasi three-dimensional magnetic nanoparticles arrays [11].

2. THEORETICAL APPROACH

Small metallic particles above the so-called blocking temperature are in superparamagnetic state and magnetization can relax by the Néel relaxation, a thermal disorder process. It is caused by the reorientation of the magnetization vector inside the magnetic core against an energy barrier [12].

In a superparamagnetic state, the direction of the particle magnetic dipole moment thermally fluctuates with a characteristic relaxation time τ, determining a period in which the magnetic moment spends in a particular direction [13]. In the absence of an applied magnetic field and interaction effects between the particles, the relaxation time can be expressed by the Arrhenius-Néel formula [14]

$$\tau = \tau_0 \exp\left(-\frac{E_B}{k_B T}\right) \qquad (1)$$

where E_B is the anisotropy energy barrier separating two easy directions of the magnetization, k_B is the Boltzmann constant, T is temperature and τ_0 is the temperature and field independent pre-exponential factor, which is in order 10^{-10}s for maghemite nanoparticles. If τ is shorter than a characteristic measuring time τ_m, the maghemite nanoparticles exhibit superparamagnetic fluctuations of the magnetic moment. When the temperature falls bellow the blocking temperature T_B, the thermal energy is smaller than the anisotropy energy barrier. It leads to a blocking of the particle magnetic moment in a particular direction (see Fig. 1).

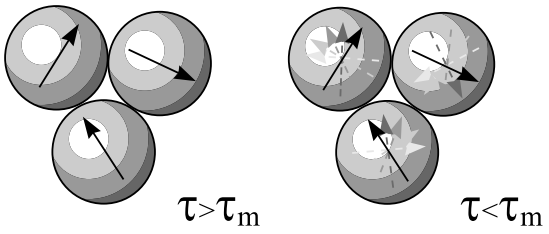

Fig. 1. Schematic illustration of blocking temperature effect: (left view) blocking state, (right view) fluctuating state.

According to the Néel-Brown relaxation model for isolated particles, the blocking temperature T_B can be expressed as

$$T_B = \frac{KV}{k_B \ln(\tau_m f_0)} \qquad (2)$$

where K is the anisotropy constant, V is the volume of each particle, τ_m is the measurement time, and f_0 is the frequency factor. In case of superparamagnetic γ-Fe_2O_3 nanoparticles of size 15nm or smaller, large differences in their magnetic properties were found [15-17]. For a maghemite nanoparticle in our experiment we chose K=10^5 J/m^3 [18], τ_m=100 s [19] and f_0=10^{12} s^{-1} [20].

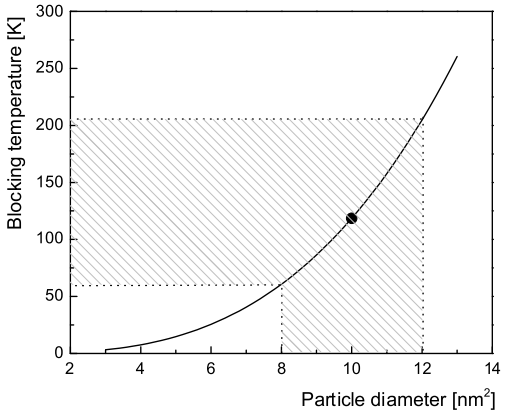

Fig. 2. Particle distribution and blocking temperature calculated from Eq. (2) for various particle diameters. Particle distribution was estimated by scanning electron microscopy at 10±2nm (for details see section 4.2).

Recent publications reported on physical properties of two-dimensional close-packed arrays of microscopic uniformity extending to the cm scale, which were formed using the Langmuir-Blodgett (LB) technique [21]. Similar close-packed arrays were recently used for magnetotransport and magneto-optical experiments [22].

3. MATERIALS AND SAMPLE PREPARATION

The Langmuir-Blodgett (LB) technique has been used to produce two-dimensional arrays of organically functionalized nanoparticles of γ-ferrite (maghemite) approx. 10 nm in diameter encapsulated in oleic acid envelope [23]. The nanoparticles dissolved in chloroform were added in small quantities (cca. 1.3 µg/µl) onto the water surface. After evaporation of the volatile solvent the particles spontaneously formed a Langmuir monolayer at the air/water interface. The π-A isotherm proved suitable stability of the monolayer as far as 30 mN/m which corresponds to a solid 2-dimensional state. The limiting area per a nanoparticle was about 100 nm^2, which is in good agreement with a scanning electron microscope figure at 1M magnification (Fig. 7).

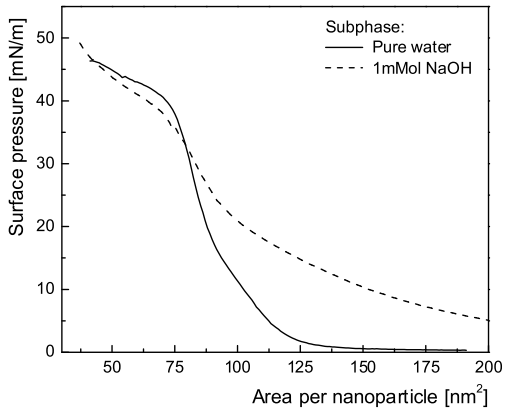

Fig. 3. Surface pressure-area isotherm of Langmuir film consisting of nanoparticles onto pure water and 1mMol NaOH subphase (pH=11).

For preparation of defect free nanoparticle layers it was necessary to hydrophobize the substrate (silicon wafer) surface. A self-assembled 1-hexadecane thiol monomolecular film on an evaporated gold layer was formed for this purpose (Fig. 3). Alternatively, a silanized silicon wafer was used as a substrate for magneto-optical measurements. The transfer of the monolayer onto a solid substrate was performed in a LB trough by vertical dipping at surface pressure of 10 mN/m. Two types of monolayer were used: pure nanoparticles and nanoparticles—stearic acid mixture.

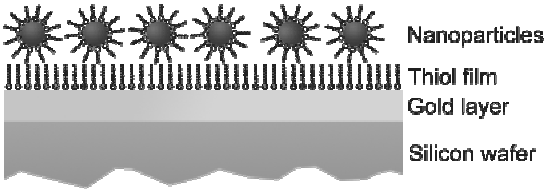

Fig. 4. Sketch of the nanoparticles layer structure.

4. EXPERIEMNTAL RESULTS

Various surface analysis techniques were applied for measurement of physical and structural properties of a planar array of magnetic nanoparticles. Magnetic properties were investigated by using magneto-optical Kerr effect. Surface arrangement was studied by scanning electron microscopy as well as atomic force microscopy.

4.1 Magneto-optical kerr effect

Kerr [24] observed that a ferromagnetic medium may effect the polarization or the intensity of polarized light when reflected by its surface. This

phenomenon, so-called magneto-optical Kerr effect (MOKE), using visible light has become a standard tool for investigating magnetic systems. Twenty years ago Moog and Bader [25] applied this technique as a surface sensitive method in investigations of thin magnetic layers. Today, advanced experimental techniques allow a sensitivity of a few atomic monolayers and planar systems of magnetic clusters embedded in non-magnetic matrices [26-27]. Using linear polarized light the specimen can be analyzed in the longitudinal case (see Fig. 5), an external magnetic field is applied in the in-plane configuration parallel to the plane of incidence.

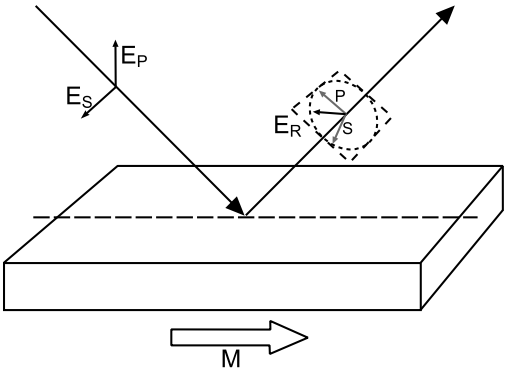

Fig. 5. Schematic view of experimental setup for MOKE in longitudinal configuration (S and P are transversally electric and transversally magnetic mode, respectively).

The respective in-plane magnetization component causes a rotation of the polarization plane combined with a change in the ellipticity which can easily be detected by the polarizing microscope (analyzer). Due to the variation of the magnetic field strength it is possible to measure the magnetization reversal during a hysteresis cycle.

As revealed by the magnetization curves measured by investigating the longitudinal MO Kerr effect the films deposited on the silanized silicon behave as superparamagnetic at the room temperature: they do not exhibit a significant hysteresis.

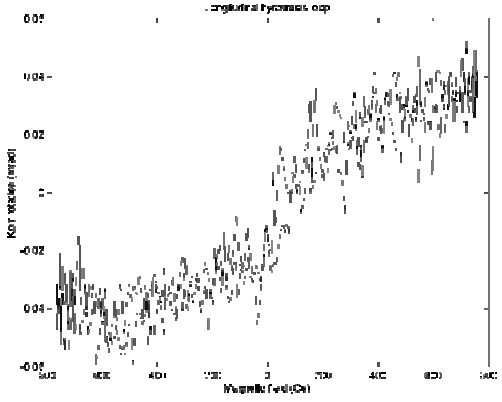

Fig. 6. The measurement of hysteresis by the MO Kerr effect in longitudinal arrangement.

4.2 scanning electron microscopy

Scanning electron microscopy (SEM) provides an ideal opportunity to the observation of ordering of conductive nanoparticles in a planar isolating matrix. The SEM measurement confirms homogeneity of the particle coating of all samples. All specimens exhibit low density of defects in the monolayer, a local defect is induced by the surface roughness (see Fig. 7, top). For a nanoparticles-stearic acid mixture a creation of stearic acid domains is observable (not shown here). A particle mean-size is estimated at 10±2nm.

The specimen with silanized surface the islands in case of deposited particles have short range order as shown in Fig. 7 (bottom) in the insert (2-dimensional fast Fourier transform (FFT) calculation).

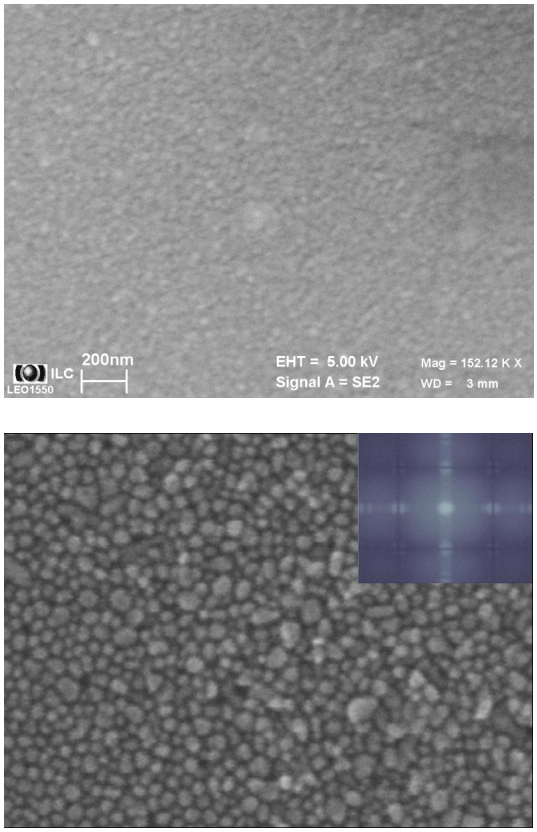

Fig. 7. Scanning electron microscope images. High homogeneity and short range order is observable (2D FFT is shown in the insert).

4.3 atomic force microscopy

Atomic force microscopy (AFM) provides additional information about the arrangement of particles on the surface. AFM measurement (see Fig. 8) exhibits minimum surface roughness and defect distribution. The height of surface undulations is quantized (one step is approx. 4 nm) and is caused by scanning across a different number of deposited layers onto the substrate.

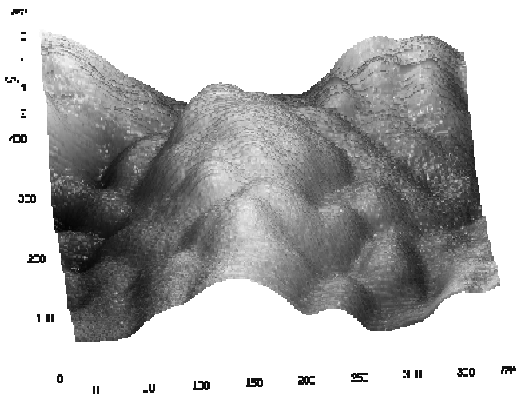

Fig. 8. AFM image of specimen surface. The surface undulations are caused by scanning across a different number of deposited layers onto the substrate.

5. DISCUSSION

Two-dimensional systems of γ-ferrite (maghemite) nanoparticles were prepared by the Langmuir-Blodgett technique. The magneto-optical Kerr effect measurements confirm a superparamagnetic behaviour at room temperature. SEM as well as AFM confirmed homogeneity of the distribution for various deposition conditions and observed the short-range order in the nanoparticles arrays.

Scanning electron microscopy verifies the assumed mean particle size to 10±2nm. The particle diameter distribution leads to a wide blocking temperature range.

The LB technique proved its versatility also for the preparation of ultradense planar magnetic nanoparticle arrays. One nanoparticle contains approx. 100 ferrite molecules and 10^{12} bits per cm^2 can be stored in the ordered layer providing a capacity, which is higher by 1 or 2 orders of magnitude than that in contemporary computer memory elements.

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