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Deposition of thin films of a transition metal complex by spin coating

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Abstract

Spin coating is demonstrated to be a promising technique for depositing magnetic transition metal complexes. The thin films show nano-crystalline formations with random orientations. The optical properties determined using spectroscopic ellipsometry compare well to those of single molecules in solution indicating the preservation of the molecular structure upon the deposition process.

1. Introduction

Most magnetic materials which are currently used in technological applications are metals, alloys or simple inorganic compounds. In the striving for higher storage densities the so-called 'bottom-up' approach, *i.e.* the molecule based formation of storage devices, increases in importance. Molecules which have a magnetic moment could replace the currently used magnetic domains leading to higher magnetic storage densities. Further technological applications of magnetic molecules such as magneto-strictive sensors, spintronic components, and magneto-optical data processing units will arise when thin films, multi-layers or nano-structures with well defined physical properties will be produced [1].

The search for magnetic molecular materials is driven by their broad chemical variety resulting from the flexibility of carbon chemistry and the structural variety of coordination compounds (for recent reviews see *e.g.* [2–4]). Bis(oxamato)metal complexes have been extensively used as versatile building blocks for homo- and hetero-polymetallic systems [5–7]. Recently, a Cu(II) containing three nuclear transition metal complex: $[Cu_3(opba)(pmdta)_2](NO_3)_2$ (Fig. 1) which exhibits a spin doublet ground state at temperatures below 30 K was synthesized [8]. This spin doublet state is due to an antiferromagnetic superexchange interaction between the Cu centres mediated by the oxamato group [8].

In order to produce thin films of molecule based materials on different substrates various deposition methods are available [9–11]. Films of ferrimagnetic 3-dimensional coordination networks such as hexacyanoferrate complexes or $V(TCNE)_x$ (TCNE = tetracyanoethylene) were fabricated by means of electrochemical deposition [12,13] and chemical vapour deposition [14,15], respectively. However, merely the Langmuir–Blodget method [16] and simple dipping into a solution have been used so far to obtain films of paramagnetic transition metal complexes [17]. The Langmuir–Blodget method provides a very good homogeneity of the films and thickness control of the order of one monolayer, but it requires the presence of special functional groups in the molecule/complex. The dip-in method should be applicable for all soluble molecules/complexes but leads to the formation of inhomogenous films with thickness of the order of micrometers. If the molecules are soluble in common solvents thin films can be produced using the spin coating method [18]. Despite the simplicity of the method, no reports exist to our knowledge on spin coated films of magnetically active transition metal complexes.

In this work thin films of the newly synthesized complex $[Cu_3(opba)(pmdta)_2](NO_3)_2$ with film thicknesses ranging from 20 nm to several hundreds of nanometres were produced for the first time on Si(1 1 1) covered with natural

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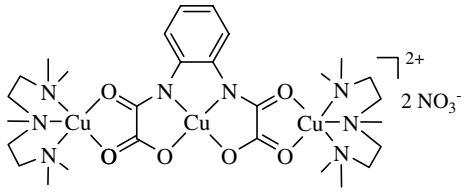

Fig. 1. Lewis formula of $[Cu_3(opba)(pmdta)_2](NO_3)_2$ with pmdta = 1,1,4,7,7-pentamethyldiethylenetriamine and opba = ortho-phenylenebis(oxamato). Note that the terminal ligands span a 3-dimensional geometry with a stretched trigonal bipyramidal coordination geometry.

SiO_2 using spin coating. We show that such films have a better homogeneity compared to films produced by simple dipping of the substrates into a solution containing the complex followed by drying under atmospheric conditions after extraction from the solution. By comparing the optical properties of the films with those of the diluted complex in solution we deduce that the molecular structure of the complex remains unaffected by the deposition process. Moreover, knowledge of the optical properties of films is of prime importance for understanding, *e.g.* their magneto-optical properties.

2. Experimental

In order to synthesize $[Cu_3(opba)(pmdta)_2](NO_3)_2$ (Fig. 1) $[Cu(pmdta)](NO_3)_2$ was coordinated on $(^nBu_4N)_2$-[Cu(opba)] where $^nBu = {}^n$butyl. The synthesis path for $[Cu_3(opba)(pmdta)_2](NO_3)_2$ is described in detail elsewhere [8]. The purity of the powder was proved using elemental analysis.

The films were deposited on Si wafers (8×8 mm) covered with 2 nm thick natural SiO_2 using spin coating. For this purpose $[Cu_3(opba)(pmdta)_2](NO_3)_2$ was dissolved in acetonitrile. The film thickness was controlled by variation of two parameters: the concentration and the rotation speed. The values are given in Table 1 for the case of two samples discussed in this work. The error bars in the third column were obtained from several experiments with the respective concentration and rotation speed. For comparison a film of approximately 100 nm was spin coated on quartz substrate.

Spectroscopic ellipsometry investigations were performed using a variable angle spectroscopic ellipsometer (VASE, Woollam Co.). Absorption measurements in solution were performed using 4×10^{-5} M solution of $[Cu_3(opba)(pmdta)_2](NO_3)_2$ in CH_2Cl_2. The measurements on solution and on the film on quartz were acquired with a Carl Zeiss Specord M40 spectrometer. Polarized optical microscopy investigations were performed with a Zeiss Axioscop 40 device. The Raman spectra were recorded in a backscattering scattering geometry using a Dilor XY 800 spectrometer equipped with a Peltier-element cooled CCD detector.

Table 1
Layer thicknesses of spin coated films determined using spectroscopic ellipsometry

Concentration (mg/ml)	Rotation speed (rpm)	Layer thickness (nm)
3	1000	30 ± 10
5	600	100 ± 20

3. Results and discussion

In order to optimize the homogeneity of spin coated films with respect to the uniformity in film thickness over the whole sample several solvents were employed. The most important criteria are good solubility and spreading of the solution on the sample surface. $[Cu_3(opba)(pmdta)_2](NO_3)_2$ exhibits high solubility in dimethylsulfoxide, *N*,*N*-dimethylformamide and acetonitrile. The latter is the most suited solvent since it has the best spreading properties on the Si/SiO_2 substrate among the mentioned solvents and a comparatively low boiling point (82 °C).

Different rotation speeds were used for the preparation of the films on Si/SiO_2 ranging from 60 rotations per minute (rpm) up to 1000 rpm in order to vary their thickness. Polarisation microscopy images measured in reflection are displayed in Fig. 2 for the films produced by dipping the substrate into a solution and using spin coating with 1000 rpm rotation speed. Fig. 2a,c were taken in non-polarized, while Fig. 2b,d were obtained in polarized mode.

For the films produced by dipping into a solution the formation of preferentially ordered needle shaped crystals with lengths of the order of 200 μm was observed (Fig. 2a). The crystalline nature of these structures is confirmed by their appearance in the polarised microscope mode (Fig. 2b) [19]. The image recorded in non-polarised

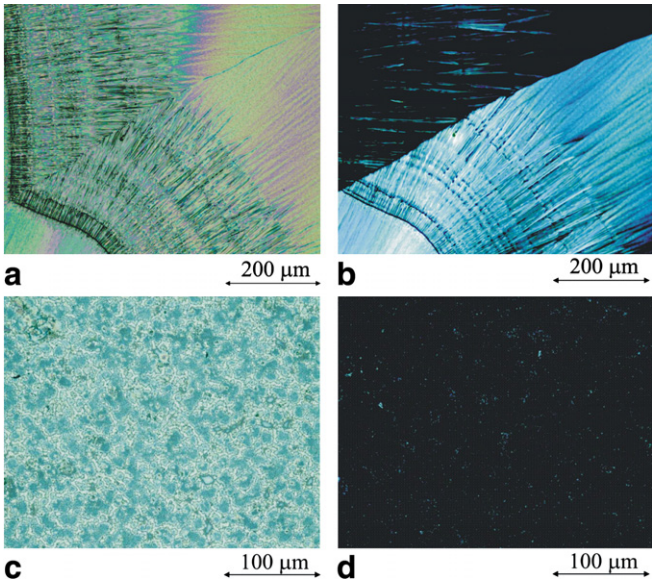

Fig. 2. Polarization microscopy images of $[Cu_3(opba)(pmdta)_2](NO_3)_2$ on $Si(1\,1\,1)/SiO_2$ using unpolarized (a)/(c) and polarized light (b)/(d), respectively, for a film produced by dipping into a solution (a)/(b) and a sample spin coated with 1000 rpm (c)/(d).

mode from the sample coated at high rotation speed (Fig. 2c) clearly shows the alternation of bright and dark areas with size in the order of only a few microns. The absence of bright regions in the image Fig. 2d recorded using polarized light reflects that only a few areas have a crystalline nature at the micrometer scale given by the resolution of the polarisation microscope. It must be noted, however, that on the nanometer scale small crystals without a preferential orientation were observed using scanning electron microscopy (Fig. 3).

The thickness of the films was determined by means of spectroscopic ellipsometry (SE). In addition, SE delivers valuable information concerning the absorption behaviour of the molecules on the substrate [20]. The film thickness was determined using a Cauchy model in the spectral range from 0.8 to 1.0 eV. The obtained values are given in Table 1. The slight absorption in this range was taken into account using a k-value of 0.1. The dielectric function in the range from 0.8 to 5 eV was evaluated considering the layers as isotropic. In a first step a point-by-point fit of the measured ellipsometric angles Ψ and Δ was performed, *i.e.* fitting the calcutated ellipsometric parameters to the experimental data at each wavelength separately. In the next step a sum of Gaussian oscillators was used to simulate the line shape of the imaginary part of the dielectric function ε_2, while the real part of the dielectric function ε_1 is generated according to the Kramers–Kronig relation. The extinction coefficient k is calculated from the complex dielectric function according to $(n + ik)^2 = \varepsilon_1 + i\varepsilon_2$, where n is the refractive index of the material. Fig. 4 shows k compared to the absorption spectrum recorded for a film on quartz with a thickness of approximately 100 nm and to that of $[Cu_3(opba)(pmdta)_2](NO_3)_2$ diluted in a CH_2Cl_2 solution (10^{-5} M).

The fine structure of the main absorption band in the solution spectrum occurs as a result of vibrational transitions which accompany the electronic transitions [21]. The intermolecular interactions in the solid state broaden the vibronic fine structure and consequently they are neither resolved in the absorption spectrum of the film on quartz, nor in the k spectrum of the film on Si. The latter two are very similar, reflecting a similar structure of the films deposited on the two substrates. This is not surprising considering that the Si substrates are covered with natural oxide.

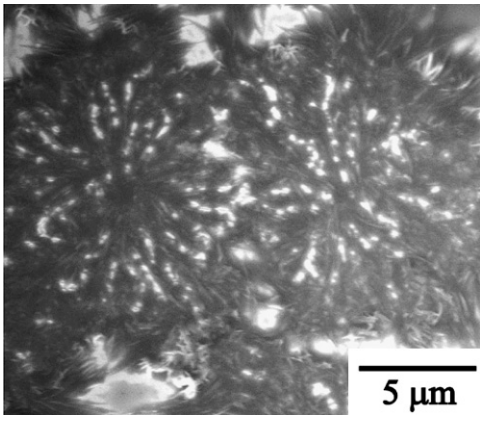

Fig. 3. Scanning electron microscopy image of $[Cu_3(opba)(pmdta)_2](NO_3)_2$ on Si(1 1 1)/SiO_2 shows nano-crystalline order.

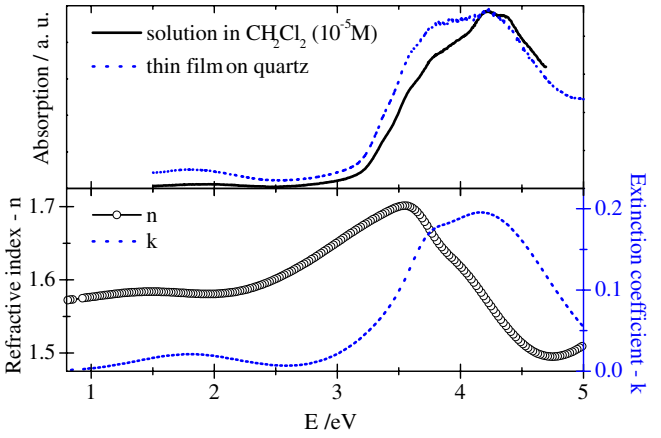

Fig. 4. Comparison between the absorption spectra of $[Cu_3(opba)(pmdta)_2](NO_3)_2$ in CH_2Cl_2 solution and of a thin film of the same complex on quartz (top). The spectra were normalized to the height of the peak at 4.23 eV. In the lower part the refractive index and the extinction coefficient for the complex as derived from the SE spectra of the thin film $[Cu_3(opba)(pmdta)_2](NO_3)_2$ on Si(1 1 1)/SiO_2 is plotted.

As a general trend we observe a red shift of the most intense absorption bands when going from the diluted solution to the solid state. The first absorption band, which is assigned to a d–d transition of Cu(II), shifts from 1.9 to 1.8 eV. The bands stemming from the charge transfer transitions at 3.5 to 4.5 eV show a red shift as well. A similar red shift of the optical absorption bands was reported for many molecules. For example, in the case of tris(8-hydroxyquinoline)-aluminum(III) (Alq_3) [22], the red shift occurs as a result of the molecular interaction in the condensed state according to Gordan *et al.* [23].

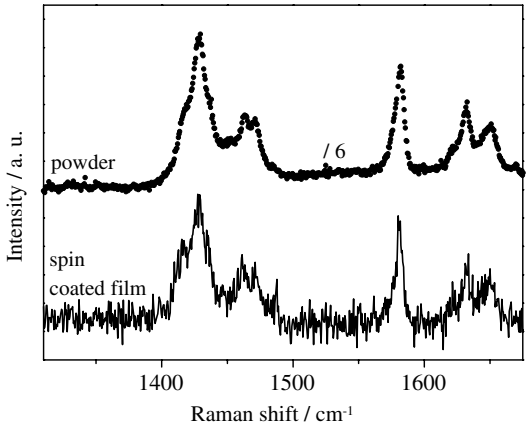

Fig. 5. Comparison between the Raman spectra measured on powder (upper spectrum) and on a thin spin coated film on Si(1 1 1)/SiO_2 (lower spectrum). The spectra are normalised to the height of the mode at 1580 cm^{-1}.

When the broadening and the red shift are taken into account the line shape of the absorption spectra of solution and thin films on quartz appear to be quite similar. This leads to the conclusion that the molecular structure is preserved during the deposition process. The finding is supported by the results of Raman spectroscopy measurements on powder and thin films. Fig. 5 displays the Raman spectra of powder and of a thin spin coated film in the region of C–H deformation and C–C, C=O, and C–N stretching vibrations where the signal is most intense. A detailed assignment of the vibrational bands will be provided in a forthcoming paper. The spectra were recorded at room temperature with the 457 nm (2.7 eV) emission line of an Ar^+ laser which lies in the absorption onset of the charge transfer band. The incident laser power was 5 mW and the laser spot size on the sample was approximately 300 μm in diameter. The resulting power density was low enough to avoid damage to the samples. A close look at the two spectra shows that the band positions as well as their relative intensities are the same, a clear proof for the preservation of the molecular structure.

4. Summary

The spin coating was demonstrated to be a promising deposition technique for magnetic transition metal complexes. The spin coated thin films of $[Cu_3(opba)(pmdta)_2](NO_3)_2$ show the formation of a nano-crystalline phase without preferential orientation leading to an isotropic optical response. The good correlation between the absorption measurements on quartz and the transmission investigations in solution reinforces the results on the optical isotropy of the films.

In general, most of the synthesized transition metal complexes cannot be sublimed. This fact might restrict their application potential in devices consisting of thin films where a very precise control of the film thickness is required. However, a lot of these compounds are soluble in common solvents and should preserve their molecular structure during the deposition using spin coating. We have shown for the case of $[Cu_3(opba)(pmdta)_2](NO_3)_2$ that a good control over the thickness and the homogeneity can be achieved by this method.

The structure of Bis(oxamato)metal complexes allows several tools for tuning their physical properties: by varying the central *N*,*N*′-bridge, the terminal ligands, and the transition metals. Taking advantage of the high flexibility of these compounds the film quality can also be adjusted eventually providing access towards technological applications.

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