

## Materials Research

### In-situ Investigation of the Crystallization of Molecular Thin Films Under Controlled Humidity

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#### Background

Phase change materials (PCM) are extensively used in different fields of technology including rewriteable data storage, display devices, sensors, mechanical actuators, and so forth. In many cases these materials are integrated into functional devices as thin films by means of different vacuum- or solution-based deposition methods. Obviously, the details of the deposition conditions dictate to a large extent the crystal structure and morphology of the PCM film, which in turn affect their phase change properties. To optimize PCM properties deposition processing parameters are not always sufficient and post-deposition treatments are often necessary. To this aim thermal annealing, which consists of heating the entire sample, is the most widespread approach. However, this may cause undesirable changes in other parts of the device.

Recently, solvent vapour annealing has been increasingly employed, in particular in the field of organic electronics, as a low-temperature alternative to thermal annealing. Solvent molecules in vapour state can interact with the surface of a material and may also diffuse into it. This leads to the weakening of interactions between the building blocks (e.g. van der Waals bonds between molecules), which become more mobile and the metastable material can thus evolve into a thermodynamically more stable state: it can crystallize, phase separate, and so forth. Nevertheless, solvent vapour annealing is a complex process, which may result also in undesirable effects, such as swelling, delamination and structural damage. The annealing must therefore be optimized

by adjusting the nature and the concentration of the solvent molecules, the temperature of the substrate as well as the duration of the solvent exposure.

In our laboratory we fabricate and investigate molecular PCMs, displaying the so-called spin crossover (SCO) phenomenon. These transition metal complexes of iron, cobalt, manganese or chromium ions are capable of undergoing reversible change between two phases (low spin and high spin) and can therefore serve as active materials for storing and processing information as well as for transducing different forms of energy in sensors and actuators [1]. Recently, we succeeded in depositing thin films of the SCO compound  $[\text{Fe}(\text{HB}(\text{tz})_3)_2]$  (tz = triazolyl) by thermal evaporation and we discovered that a simple water-vapour annealing process can induce drastic morphological and structural rearrangement within the as-deposited film [2]. The water vapour annealed films showed dramatically improved SCO properties, in terms of stability, reproducibility and sharpness. The Linkam instrumentation played a crucial role in this research. Not only was it used for ex-situ spectroscopic measurements to evaluate the process efficiency, but also the transformation between the as-deposited amorphous film and the stable crystalline film could be followed in-situ under controlled humidity and temperature conditions.

#### Method

The bulk powder of  $[\text{Fe}(\text{HB}(\text{tz})_3)_2]$  was heated until 250 °C and evaporated at a rate of 0.003 nm/s at a base pressure of  $2 \times 10^{-7}$  mbar to grow films with a nominal thickness of ca. 100 nm on fused silica substrates. The as-deposited films were then exposed to water vapour using a Linkam THMS600-H stage in conjunction with an RH95 humidity controller. The UV absorbance of the films was followed in-situ during the solvent annealing process by means of a UV-VIS spectrophotometer. The SCO properties of the annealed films were controlled using the same Linkam stage in conjunction with Raman spectroscopy. The surface topography of the films

was analysed by means of atomic force microscopy (AFM) and their crystallinity was established by x-ray diffraction (XRD).

## Results

The crystallinity of the films of  $[\text{Fe}(\text{HB}(\text{tz})_3)_2]$  impacts considerably their UV absorbance (Fig. 1a), a phenomenon, which can be used to monitor in-situ the effect of solvent annealing. Figure 1b shows such experiments, which were conducted at different temperatures when increasing the relative humidity (Rh) from 43 % to 90 % in the Linkam THMS600-H chamber. Crystallisation was observed only at low-temperatures ( $< 40\text{ }^\circ\text{C}$ ) and the best results were obtained near room temperature. Notably, at  $25\text{ }^\circ\text{C}$  when the relative humidity is gradually increased by the RH95 controller a very abrupt jump of the absorbance (ca. 10 sec in duration) was observed, which corresponds most likely to a film crystallization process by nucleation and growth.

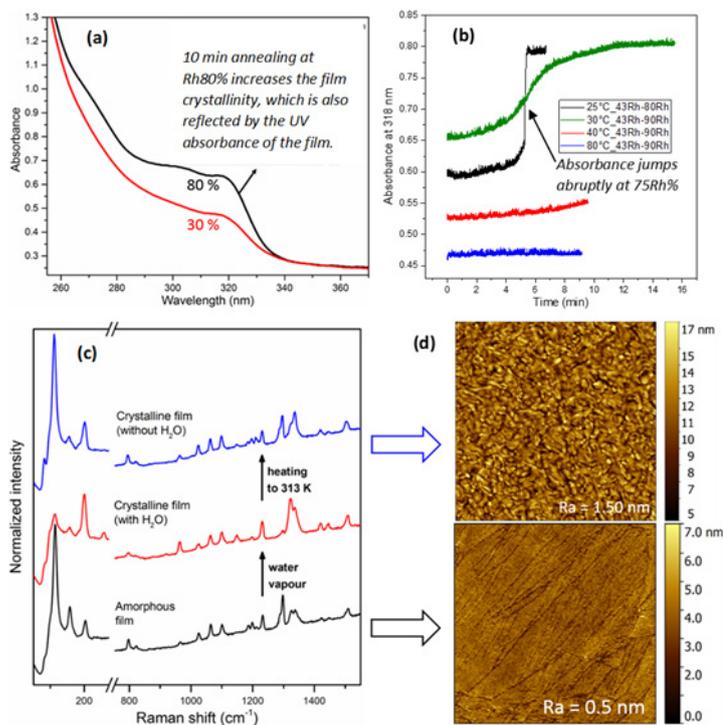
This transformation was found irreversible indicating the formation of the thermodynamically stable film. Following the water vapour annealing process the films are hydrated, but in-situ Raman spectroscopic monitoring revealed that a gentle heating to  $40\text{ }^\circ\text{C}$  allows to remove the water content (Fig. 1c). A protocol was then established (10 min annealing at  $25\text{ }^\circ\text{C}$  in Rh80% followed by 5 min annealing at  $40\text{ }^\circ\text{C}$  in ambient air) leading to dehydrated, crystalline films of  $[\text{Fe}(\text{HB}(\text{tz})_3)_2]$ , which are smooth and homogeneous with no appreciable pinholes (Fig. 1d).

films when increasing the relative humidity from 43 % to 90 % at different substrate temperatures (25, 30, 40 and  $80\text{ }^\circ\text{C}$ ). (c) Raman spectra of a film acquired subsequently (from bottom to top) on the pristine film, after water vapour annealing and after heating to 313 K. (d) AFM surface topography images of the initial (amorphous) and final (crystalline) films. Image size is  $10\times 10\text{ }\mu\text{m}^2$ . (Reproduced from Ref. 2 with permission from The Royal Society of Chemistry).

## References

[1] G. Molnár, S. Rat, L. Salmon, W. Nicolazzi, A. Bousseksou, Spin Crossover Nanomaterials: From Fundamental Concepts to Devices, Adv. Mater. 2018, 30, 17003862.

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**Figure 1.** (a) UV absorbance spectra of the pristine and water vapour annealed films. (b) In-situ monitoring the UV absorbance of  $[\text{Fe}(\text{HB}(\text{tz})_3)_2]$