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Thin films of a ferroelectric phenazine/chloranilic acid organic cocrystal

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A B S T R A C T

Phenazine–chloranilic acid cocrystal thin films can be formed by vacuum evaporation of the component molecules onto cooled substrates. Fluxes of phenazine and chloranilic acid were provided from separate sublimation sources, from which the cocrystalline phase can be formed under a wide range of impingement rates of the component molecules. Substrates consisted of Au or Ni thin films on Si wafers, cooled to 100–140 K during deposition. X-ray diffraction and scanning electron microscopy show that this process yields polycrystalline thin films of the cocrystal with voids between crystalline grains. The relative intensities of X-ray reflections differ from reported intensities of polycrystalline powders, suggesting that the films have an anisotropic distribution of crystallographic orientations. The cocrystalline thin films have an effective dielectric constant of 13 at room temperature, increasing at lower temperatures and exhibiting a broad maximum near 200 K. The means to grow thin films of organic ferroelectric materials will allow the integration of new functionalities into organic electronic device structures, including capacitors and field-effect transistors.

1. Introduction

Organic ferroelectrics based on two-component molecular cocrystals promise to expand the range of dielectric functions available in organic electronics [1]. Among useful ferroelectric properties are a remnant electrical polarization in the absence of an externally applied field, piezoelectricity, and a large dielectric constant. Existing thin-film organic ferroelectric materials such as ferroelectric polymers exhibit a remnant polarization and thus have many of the desirable properties of the broader class of ferroelectrics [2–4]. The range of opportunities available with these ferroelectric materials, however, would be broadened by the development of thin films exhibiting the divergence in properties observed at displacive phase transitions, a phenomenon that has not been available in ferroelectric polymers. The appropriate displacive ferroelectric–paraelectric phase transitions are observed in molecular cocrystal ferroelectrics, and can lead to large enhancements in electrical properties such as dielectric constants, exactly as in inorganic ferroelectrics [1,5]. These properties have the potential to be the basis for improved non-volatile memories, pyroelectric infrared detectors, mechanical actuators, dielectric phase shifters, and high-dielectric-constant gate insulators [5]. Varying the Curie temperature of a displacive ferroelectric by modifying its composition, for example, would allow the properties of the dielectric and ferroelectric phases to be tuned for specific applications [6].

The potential benefits arising from the development of a thin film form of organic ferroelectric cocrystals include the manipulation of polarization in multilayers and superlattices, the creation of functional heterogeneous interfaces with organic semiconductors and other electronic materials, and exploitation of size effects in nanostructures. Similar motivations have driven the creation of oxide ferroelectric thin films and heterostructures [5]. Here we report the fabrication and properties of thin films of a phenazine (Phz)–chloranilic acid (H_2ca) cocrystal. Phz–H_2ca is the prototypical compound in the class of materials described by Horiuchi et al. [1] and Saito et al. [7], exhibiting a Curie temperature of 253 K in single crystals and bulk powders. Processes forming Phz–H_2ca cocrystal thin films by vacuum deposition can take advantage of thermodynamic considerations similar to those of a few specific inorganic systems, including GaAs. The stoichiometric composition of Phz–H_2ca requires the incorporation of an equal number of molecules of each chemical component into the crystal. In molecular beam epitaxy, one often achieves the required composition via precise control of the fluxes of the component atoms [8]. In some systems, however, including GaAs, thermodynamic considerations permit a range of deposition parameters, the MBE window simplifying the design of the deposition process [9]. In that case, the thermodynamics of the phase diagram are exploited to grow the line compound in an excess of the flux of one of the components.

There is at present insufficient thermodynamic data available for the Phz–H_2ca system to allow the precise design of a deposition process under conditions analogous to the GaAs MBE

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window. For example, the vapor pressures of the Phz and H_2ca above the cocrystal, the individual vapor pressures of Phz and H_2ca, and the phase diagram of the Phz–H_2ca two-component system are not yet reported. This limitation has been overcome in the growth of other similar cocrystal compounds, for example using a solid-state reaction to convert single crystals of a single component to the phase [10]. Here we report a complementary approach that forms thin films of the desired phase using the fundamental concept that the fluxes of the two components need not be equal during growth. We show that under a range of deposition parameters it is possible to produce thin films of the Phz–H_2ca cocrystal from the fluxes of the component molecules.

2. Experimental

The Phz–H_2ca cocrystal thin films were created by thermal evaporation in vacuum onto Au or Ni thin films on a Si (0 0 1) substrate. Substrate temperatures during the deposition of the Phz–H_2ca cocrystal thin films were between 100 and 140 K. Neither the Phz–H_2ca cocrystal nor either component condenses on room-temperature substrates. The use of two separately heated effusion cells allowed independent control of the fluxes of Phz and H_2ca to the sample surface.

A series of depositions of the component molecules were conducted to characterize the formation of thin films of Phz and H_2ca separately. Typical source temperatures for H_2ca and Phz were $T_H = 90\ ^\circ$C and $T_P = 70\ ^\circ$C, respectively. These thin films of the pure components were produced to verify that the vapor deposition process did not result in the decomposition of Phz or H_2ca, and to determine the range of source temperatures over which the sources produced a useful flux of the components. X-ray diffraction patterns (Fig. 1) were acquired using θ–2θ scans on a laboratory diffractometer with Cu Kα radiation. The diffraction patterns in Fig. 1(a) and (b) show that both Phz and H_2ca form polycrystalline thin films with no unique preferred crystallographic orientation. Reflections in Fig. 1(a) and (b) match reflections from the reported structures of H_2ca and Phz [11–13]. The Phz thin film diffraction pattern in Fig. 1(b) includes signatures of both the alpha and beta polymorphs of Phz.

The Phz–H_2ca cocrystal thin film growth process began with the substrate and the source materials at room temperature and the vacuum system evacuated to a pressure of 10^{-6} Torr. The substrate was then cooled to the growth temperature, the molecular sources were heated, and deposition was started by opening the source shutters. Cocrystal thin films were most often produced at the typical source temperatures of $T_H = 90\ ^\circ$C and $T_P = 70\ ^\circ$C given above. It was also possible to produce cocrystal thin films with simultaneously lower fluxes of both molecules, with source temperatures of $T_H = 70\ ^\circ$C and $T_P = 40\ ^\circ$C. Substrate temperatures higher than the typical range of 100 to 140 K produced thin films with crystals of both the Phz–H_2ca phase and pure H_2ca.

Electrical measurements of the Phz–H_2ca films were made using thin film capacitors defined by Au top electrodes deposited through a shadow mask. The dielectric constant and dielectric loss in a Phz–H_2ca thin film on a Ni substrate were measured as a function of temperature using a capacitance bridge (Andeen-Hagerling AH 2500) with the sample in vacuum. The sample was excited with 0.75 V rms at a frequency of 1 kHz. Electrical leakage through the Phz–H_2ca cocrystal thin films was evaluated with steady-state current–voltage measurements using a semiconductor parameter analyzer (Agilent 4155C).

3. Results and discussion

X-ray diffraction patterns of Phz–H_2ca cocrystalline layers deposited onto Au and Ni thin films are shown in Fig. 1(c) and (d), respectively. Reflections near $2\theta = 15^\circ$ and $2\theta = 25^\circ$ allow the Phz–H_2ca cocrystal to be distinguished from the Phz and H_2ca components. A more detailed analysis shows that the Phz–H_2ca cocrystal exhibits X-ray reflections at angles consistent with the structure reported in the literature [14]. This result applies to

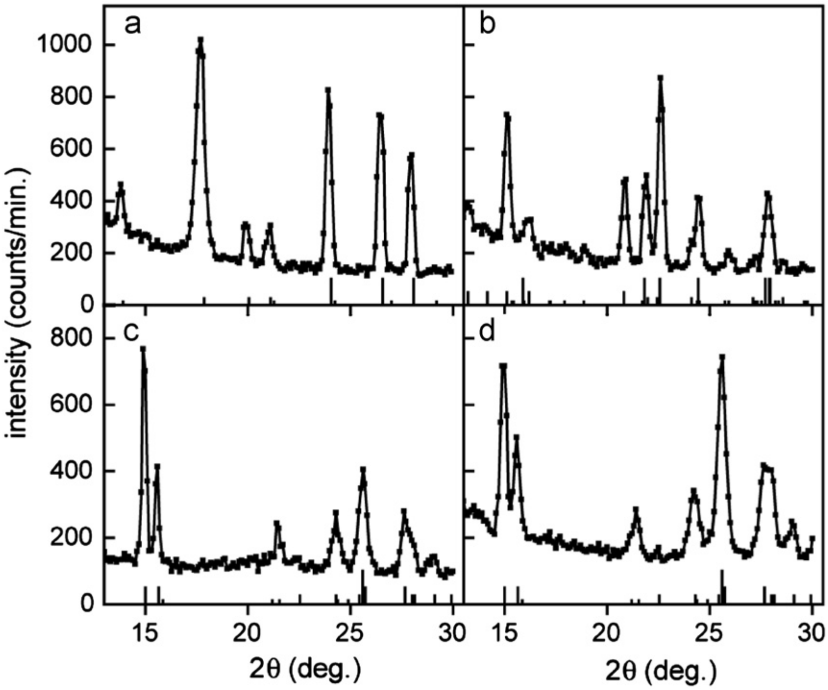

Fig. 1. X-ray diffraction θ–2θ scans with Cu Kα radiation for thin films of (a) chloranilic acid (H_2ca) and (b) phenazine (Phz) and Phz–H_2ca cocrystal on (c) Au and (d) Ni bottom electrodes. Angles associated with reflections of the reported structure of each material are represented as vertical lines with heights proportional to the intensity reported in powder diffraction studies [11–13]. Reflections for both polymorphs of phenazine appear in (b).