
Melting Behaviour Of Cdga Film Grown On Chemically Treated Si Wafer

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ABSTRACT:

The theory predicts two-step melting in thin films, from crystal to a hexatic phase and then from hexatic to a liquid phase. Melting of LB films as a function of film thickness has been extensively studied in the literature. In literature distorted hexagonal lattice structure of Cd arachidate multilayer has been reported. Existence of a hexaticlike phase has been clearly evidenced in such studies. Further, existence of an intermediate smectic or nematic phase inserted between solid and hexatic phases in a system with a distorted hexagonal symmetry, as predicted by theory, has also been observed. Even in thick films of cadmium arachidate, low dimensionality effects have been observed in the surface region. Before melting transition, the distorted hexagonal lattice structure of CdA LB film transform to hexaticlike phase with increasing temperature. This hexaticlike phase is specified by a tilting of chains in vertical direction and a decrease in the in-plane distortion.

Keywords: Melting, CdGA Film, Si Wafer.

INTRODUCTION:

Well ordered metal-organic films [1; 2] of controlled thickness [3; 4] can be prepared by Langmuir-Blodgett technique [5; 6]. Such LB films are ideal for studying the basic physics of low-dimensional systems. However, the characterization of low-dimensional structure becomes important to understand the underlying growth mechanism. This understanding helps us in fabricating new desired structures, which manifest novel physical properties for device applications [7; 8]. Low dimensional systems sometimes demonstrate completely different properties from bulk [9; 10]. Confinement effect, large surface to volume ratio and interface energies of nano-materials is the probable reasons behind this. Substrate surface condition also plays crucial role in the growth and stability of nano-layer on it [11; 12]. A promptly implemented method to improve the film quality is to alter the surface energy of the substrate to boost a better film growth. The surface and interface energies influence the structural properties

significantly, because large surface is available to react [13-16]. As the LB film contains amphiphilic molecules, having both hydrophobic and hydrophilic parts, its structure can be improved by changing the surface nature of the substrate. The modification of surface can be easily done by passivation of the substrate surface. This basically modifies the surface nature, in term of free energy or polarity and accordingly, hydro nature of the surface can be tuned. Some studies on LB film show that different types of layered structures can be grown [17-20]. In addition, marked dependence of the morphologies and the qualitative dynamics on the surface composition has been observed in blends of polystyrene and poly (methyl methacrylate) spun cast on Si, Au and Co surfaces [21]. Higher interfacial interaction resulted in an increase in the glass transition temperature of poly (methyl methacrylate) on Si and Al surfaces [22]. However, the transition temperature as well as melting temperature depends significantly on the type of layer. These results can be understood in terms substrate induced perturbation at the interface.

EXPERIMENTAL DETAILS:

Two sets of 13 monolayered (ML) CdA LB films have been deposited on silicon (100) substrates, chemically treated according to the wet passivation. Prior to the deposition, Si (100) substrates were chemically treated differently. Different treatments provide differently terminated surfaces. Si substrates were made -OH terminated after keeping them in a basic piranha solution of ammonium hydroxide NH_4OH (30%), hydrogen peroxide H_2O_2 (30%), and Milli-Q water ($\sim 18\text{MQcm}$) [$\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2=2:1:1$], for 10-15 min at 100°C . These substrates are expected to show hydrophilic nature. Another set of Si substrates which were made -H terminated by keeping them in a solution of hydrogen fluoride HF (10%) for 3 min at room temperature, are expected to show hydrophobic nature.

A LB films were deposited using Langmuir-Blodgett technique (model KSV 2000). The LB films of CdA were prepared by the vertical deposition mode. Arachidate acid (purity > 99.9%) was dissolved in chloroform (HPCL Grade) at a concentration of 1 g/L for use as the spreading solution. 70pL of solution in chloroform (HPCL grade) was spread on the subphase surface. The subphase was prepared with CdCl_2 (purity > 99.8%) dissolved in Milli-Q water (resistivity > 18MQcm) to a concentration of 0.9966 g/L and adjusted to pH 6.7 using NaHCO_3 (purity > 99.9%). LB deposition was performed at a surface pressure of 30 mN m^{-1} with a dipping rate of 3 mm min^{-1} at 20°C . The films were allowed to dry in air for 5 min after each up-stroke. The multilayers were then designated as CdA-OH and CdA-H respectively.

GID measurements have been performed at EDXRD beam line BL- 11, of INDUS-II synchrotron radiation source. Diffracted radiation is energy analyzed at fixed 2θ ($=18^\circ$) angle using high resolution HPGe detector mounted on detector arm. The

diffraction scans were performed at the fixed grazing angle of $\theta=0.2^\circ$. An exposure time of 300 s was used for taking one diffraction pattern. A miniature furnace was used for controlled heating of the sample, which was kept in ambient atmosphere. The sample temperature was maintained with an accuracy of $\pm 0.5^\circ\text{C}$. In order to avoid any influence of radiation damage during the measurements, the sample was shifted across the beam by 2 mm after each scan so that a fresh area of the film was exposed to the X-rays.

RESULTS AND DISCUSSION:

Both the reflectivity patterns show presence of well-defined Bragg peaks corresponding to the bilayer periodicity of 5.54 nm in case of CdA-OH and 5.52 nm in case of CdA-H multilayer. Visibility of more than 5th orders of Bragg peaks in reflectivity pattern suggests good quality of multilayers. However, overall reflectivity patterns of the two films exhibit subtle differences, which could be fitted by considering structural models which take into account the hydrophilic and hydrophobic nature of the Si-OH and Si-H surfaces.

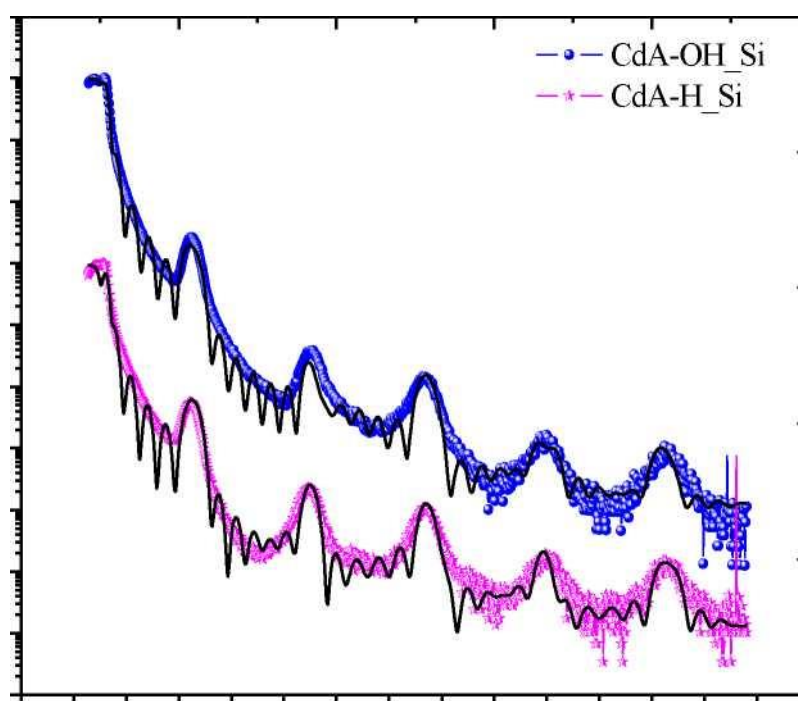


Figure 1: X-ray reflectivity of CdA LB films deposited on different chemically treated Si substrates

Figure 1 shows the X-ray reflectivity pattern of the CdA LB films deposited on different chemically treated Si surfaces, along with the best fit. The reflectivity data were analyzed using Parrett's formalism.

Langmuir-Blodgett films are inherently 2D-structures and the transfer of

monolayer film can occur via hydrophobic interactions between the alkyl chains and the substrate surface or the hydrophilic interaction between the head groups of the molecules and the substrate surface. Depending upon the nature of the substrate surface LB film follows the favorable structure, it attaches with the substrate through head for hydrophilic surface and through tail for hydrophobic surface. In CdA-OH multilayer the substrate nature was hydrophilic; CdA molecules attach with the substrate through head, which takes place during first up stroke of the deposition. While in CdA-H multilayer the substrate was hydrophobic; CdA molecules attached to the substrate through tail during first down stroke of deposition. Successive deposition on top of the first layer, simply being repeated until the desired number of layers has been deposited. These models are in conformity with those proposed in reference. The schematic view of the two monolayer stack model on differently terminated Si substrate is shown in figure 2.

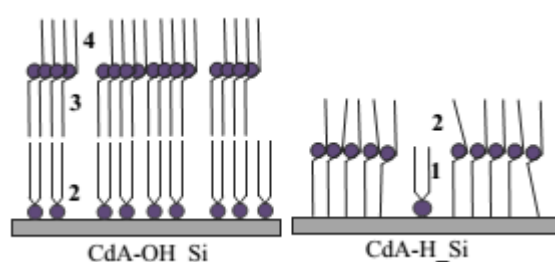


Figure 2: Schematic illustration of model structures of CdA LB films grown on differently terminated Si substrates.

The energy dispersive in-plane diffraction pattern of CdA LB film exhibits two well defined peaks around $q_{xy} = 15.6 \text{ nm}^{-1}$ and 16.6 nm^{-1} (fig. 3). The assignment of diffraction peaks is $(0\ 1\ +1\ 1)$ and (10) of distorted hexagonal lattice structure, in conformity with earlier works [169; 170; 174].

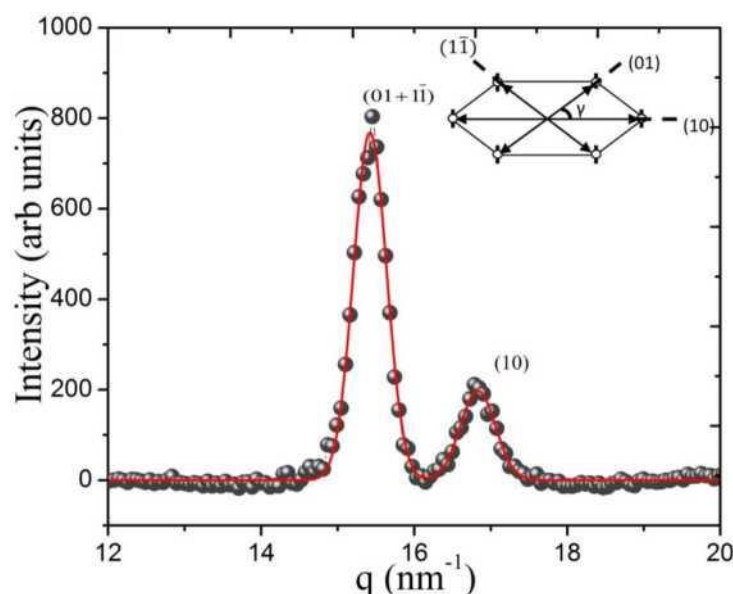


Figure 3: In-plane diffraction profile of as prepared CdA-OH LB film at room temperature, inset shows the distorted hexagonal structure and different crystallographic directions.

Figure 4 shows the temperature dependent in-plane diffraction patterns of both the films, after correcting for energy dependence of incident flux and nonlinear background. The diffraction data have been fitted with two Gaussian peaks in order to extract the temperature-dependent peak positions and their widths.

The diffraction peaks shift to smaller values of q_{xy} with increasing temperature indicating thermal expansion of lattice plane. The (10) peak shifts faster than the peak, signaling, decrease in the distortion from hexagonal lattice. As the temperature increases the peaks broaden, which reflects decrease in the coherence length.

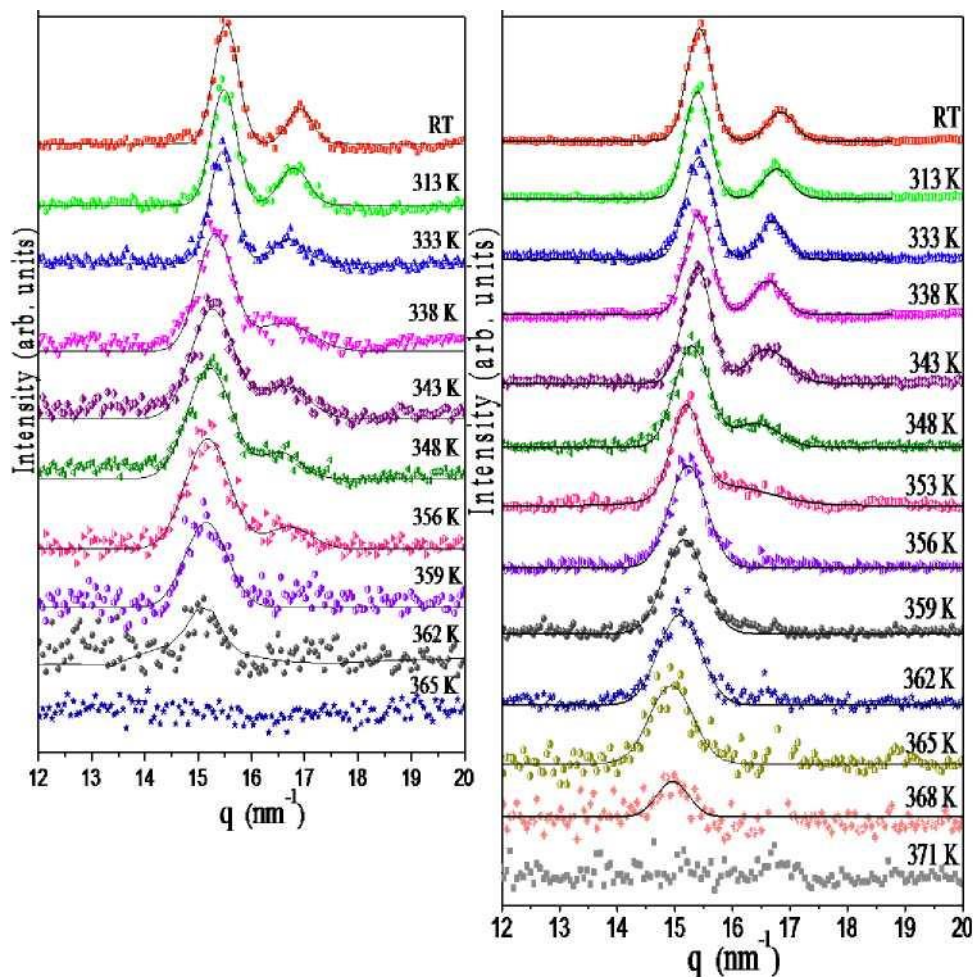


Figure 4: Temperature dependent in-plane XRD pattern of CdA LB film grown on (a) -H terminated Si substrate and (b) -OH Si substrate used to extract the temperature- dependent distortion (Δy) from the hexagonal lattice.

The distortion of the lattice from regular hexagon can be quantified in terms of parameter $Ay = 60 - \gamma$, where

$$\gamma = \cos^{-1} \frac{q_2}{2q_1} \dots \dots \dots (1)$$

with q_1 and q_2 being positions of the $(01 + \bar{1}\bar{1})$ and (10) reflections respectively.

From figure 3.5, one can see that with increasing temperature the distortion of the lattice from regular hexagon decreases and goes to zero for sufficiently high temperature. In both the films, up to a temperature of about 343 K, there is a slow variation in the distortion (Ay). In CdA-OH film distortion of the lattice starts decreasing from 343 K, while in CdA-H film the distortion of the lattice is almost unchanged upto 356 K. However, beyond this temperature distortion rapidly decreases to zero; at 359 K in CdA-H specimen and 362 K in CdA-OH multilayer. This rapid decrease in Ay signals transformation to a hexaticlike phase. The results show that the transition to hexaticlike phase occurs at lower temperature in CdA-H film then in the CdA- OH film.

Line width of a diffraction peak is an indication of the coherence length (ξ) along that direction, which can be calculated using the relation:

where $\Delta = \sqrt{\Delta_m^2 - \Delta_{ins}^2}$ is the full width at half-maximum of the diffraction peak, corrected for instrumental broadening, Δ_{ins} ($=0.22 \text{ nm}^{-1}$), and Δ_m is the experimentally measured width.

Figure 3.6 gives temperature dependence of the width of various diffraction peaks. The peaks get broadened with increasing temperature corresponds to decrease in the coherent length. One can see that an anisotropy exists between the $(01 + \bar{1}\bar{1})$ and (10) directions. With increasing temperature, the coherence length along the (10) direction decreases at a faster rate as compared to that along $(01 + \bar{1}\bar{1})$ direction, in both the films.

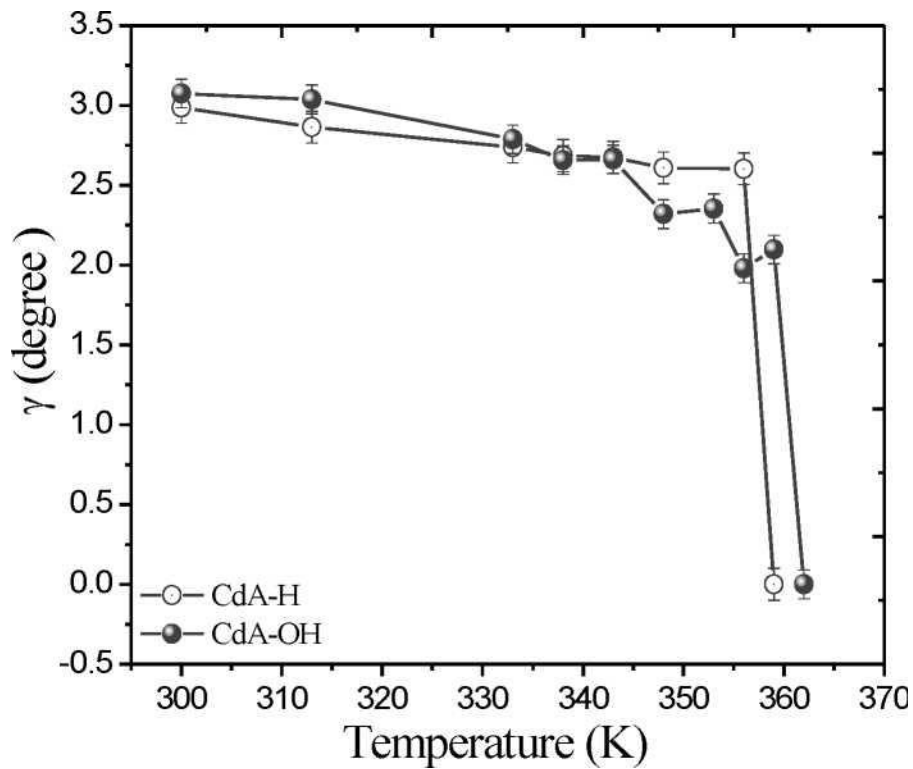


Figure 5 Lattice distortion (γ) as a function of temperature.

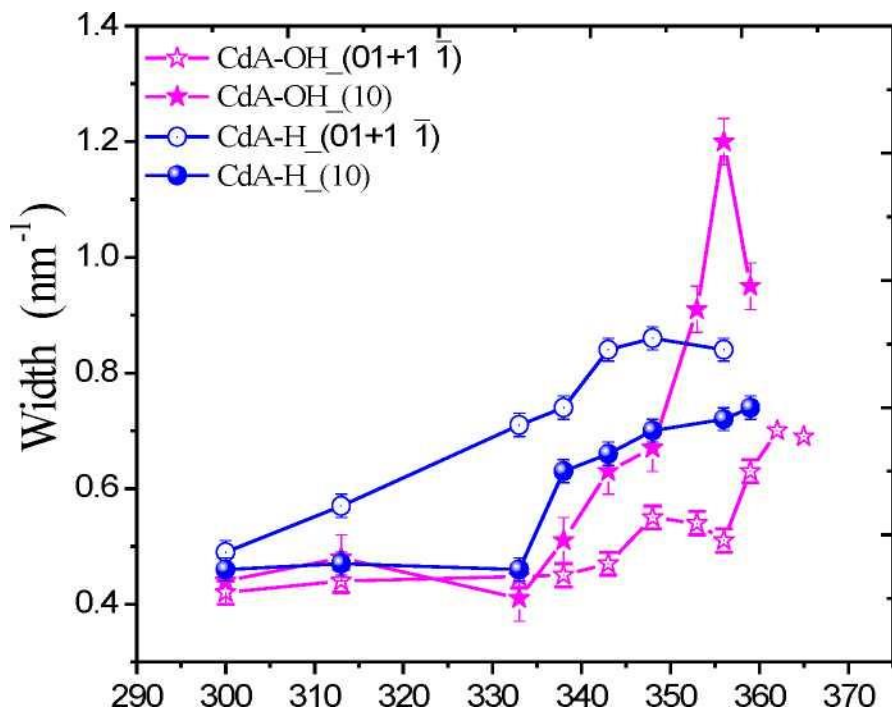


Figure 6 Temperature dependence of the width of the $(01+1\bar{1})$ and (10) peaks in CdA-H and CdA-OH.

Before complete melting of the LB film, the coherence length along the (0 1 + 1 1) direction is 4.3 and 2.9 nm, while along the (10) direction, it becomes 1.7 and 2.5 nm for the samples CdA-OH and CdA-H, respectively. This shows that the ordering in lattice plane is more in (0 1 + 1 1) direction at higher temperature.

In CdA-H multilayer the size of the coherent domains shows a continuous decrease starting from the room temperature onwards while in CdA-OH multilayer size of the coherent domains remain almost unchanged (within error) till 333 K. In the melting process of CdA LB film the domain area came down to 4.2 nm² from 13.6 nm² in CdA-OH, and to 4.1 nm² from 11.0 nm² in CdA-H, indicating the formation of smaller crystallites of the LB film (fig. 7).

The diffraction lines completely disappear around 362 K in CdA-H, indicating in-plane melting. On the other hand, in CdA-OH the diffraction lines are still visible at 365 K and disappear only above to 368 K. Thus, the melting transition occurs at a lower temperature in CdA-H multilayer as compared to the CdA-OH multilayer.

LB films exhibit substantial reorganization after transfer to the substrate. Long range order sets in after deposition of three layers, and has been attributed to head group-head group interaction. Type of substrate or subphase pH can affect the structure of the as-deposited film as well as the subsequent reorganization. Effect of hydrophobicity and hydrophilicity of the substrate on the structure of LB film has also been studied in the literature. Studies have shown that Ni-arachidate films deposited on OH and H terminated Si surface exhibit significant differences. While films deposited on OH terminated surface are quite stable with time, on H terminated Si surface NiA film shows structural instability occurring over a time scale of a few days.

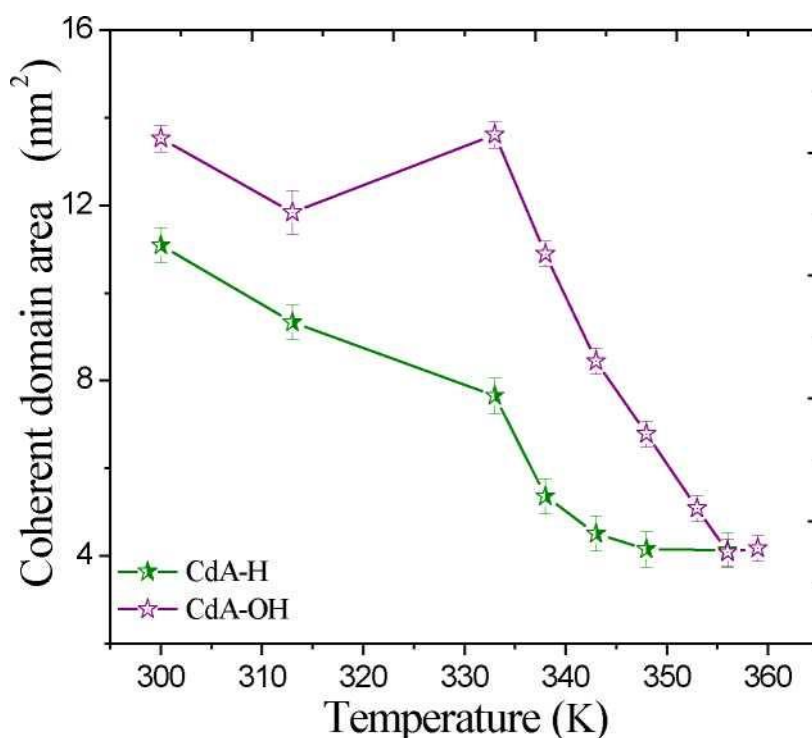


Figure 7: Coherent domain area of CdA-H and CdA-OH LB films as a function of temperature.

The observed effects have been attributed to i) growth of native oxide on the Si surface, and ii) configurational changes occurring in NiA molecules. On H terminated surface, in-plane diffusion of molecules is much more restricted as compared to that on OH terminated surface, resulting in a less compact in-plane structure. Further, configurational changes are also stirred with growth of native oxide at the Si surface. The system reaches an equilibrium structure over a period of 30-40 days. In the present case, melting behaviour of CdA films was studied several months after the preparation of the same.

CONCLUSION:

Therefore, the films are expected to have already reached equilibrium structure at room temperature. One expects a higher level of defects and imperfections in CdA-H film because of more restricted in-plane diffusion and the configurational changes occurring subsequent to the surface oxidation of Si substrate. Furthermore, raising the temperature may result in creation of further instability in the system. These imperfections and instabilities may be the cause of a faster structural transformation in CdA-H film as compared to CdA-OH film.

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