

The effect of substrate on nucleation rate of two-dimensional colloidal crystals

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Colloidal crystals have been employed for fundamental studies as it is a promising model of the phase transitions in the atomic and molecular systems. The nucleation of colloidal crystal is influenced by the substrate as the same as in the atomic system. However, the effect of substrate on the nucleation has not been quantitatively evaluated for the colloidal crystals to our knowledge. Detailed nucleation process of colloidal crystals on the cover glass has been investigated, and occurrence of two different nucleation processes has been revealed. To obtain better understandings on the substrate effect, nucleation of colloidal crystals on three different substrates, cover glass, Pt-coated and Au-coated cover glass, are examined. The nucleation rate, J , is measured for three substrates, from which the value of interfacial free energy change, $\Delta\sigma$, for each substrate is obtained.

Crystallization of colloid was induced by the depletion attraction, in which charged polystyrene particles and charged sodium polyacrylate polymer were mixed. 500 nm with green fluorescent polystyrene particles were used. Sodium polyacrylate was added in the solution as depletant to generate attractive interaction. The platinum and Au coated cover glass were prepared by sputtering deposition. Crystallization processes were monitored by optical microscopy.

Nucleation of colloidal crystals on different substrate under the same supersaturation are shown in Figure 1 (15 minutes after mixing solution). The number of grains on the Pt-coated cover glass is least among three substrates. The nucleation rate, J , is measured for three substrates as shown in Figure 2. Interfacial energy change, $\Delta\sigma$, is generated during nucleation on the substrate. The values of $\Delta\sigma$ on the cover glass, Au-coated, and Pt-coated cover glass are obtained based on equation of the classical nucleation theory (CNT) to be 0.83, 1.39, and 1.47 [$k_B T/a$], respectively, where k_B is the Boltzmann constant, T is the absolute temperature and a is the particle diameter.

The $\Delta\sigma$ is generally expressed as, $\Delta\sigma = \sigma_{\text{sub-solid}} + \sigma_{\text{solid-liquid}} - \sigma_{\text{sub-liquid}}$, where σ is the interfacial energy between each phase. Since the $\Delta\sigma$ originates from bonding energy between substrate and crystals in the atomic system, we deduce that the magnitude of $\Delta\sigma$ is related to the strength of van der Waals interaction between particles and substrate supposing that the strength of depletion interaction is the same for each substrate. The strength of interaction between particles and substrate is measured by AFM and is consistent with the order of the $\Delta\sigma$ magnitude on three substrates. The larger attractive interaction between colloidal particles and substrate yields higher $\Delta\sigma$ and hence the J is smaller.

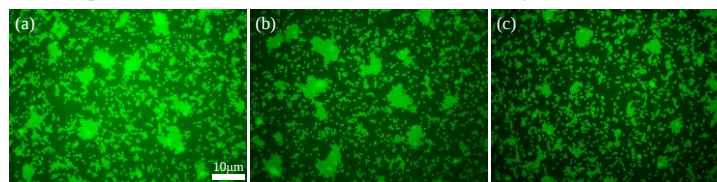


Figure 1 Nucleated 2D islands on different substrate under the same supersaturation; cover glass (a), Au-coated cover glass (b), Pt-coated cover glass (c). Volume fraction of polystyrene is 0.5%, and concentration of sodium polyacrylate is 0.15 g/L.

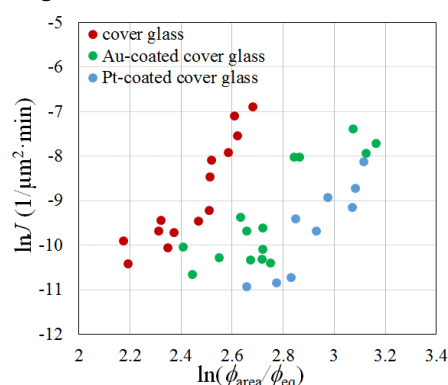


Figure 2 $\ln J$ as a function of $\ln(\phi_{\text{area}}/\phi_{\text{eq}})$ for the different substrate. ϕ_{area} is the area fraction, which corresponds to surface concentration of ad-particles, ϕ_{eq} is the equilibrium ϕ_{area} where no growth or dissolution occurs.