

Nanobubble formation in gas hydrate dissolution process and memory effect of gas hydrate recrystallization

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Gas hydrate is the ice-like crystal formed by water molecules (host lattice) and gas molecules (guests in the cages). Usually the initial nucleation of gas hydrate requires the large super saturation (or super cooling) conditions. However, the recrystallization from the solution dissociated the gas hydrate crystal requires the smaller super saturation compared to the initial one. This phenomenon is called 'memory effect' of gas hydrate formation, which is expected to be used for the industrial utilization of gas hydrates.

The mechanism of the memory effect has not been revealed yet, but several models have been proposed. One of them is considered that the cage-like structure is remaining in the dissolved solution even after the crystal dissociation. We consider that, in addition to the host lattice formation, the condensation process of guest molecules would be required for the recrystallization of gas hydrates. It is because the guest molecule concentration in the crystal is much higher than the solubility in water. As one of the possible idea of this gas condensation process, we consider that the nanobubbles would be formed when the gas hydrate is dissolved. In the gas hydrate crystal, each guest molecule is engaged in the cage. When the gas hydrate crystal is dissolved in the solution, guest molecule would be dissolved in the solution one-by-one. Thus the gas molecule aggregation formed in the solution would be small, that is, becomes nanobubble.

The Nanobubble has several unique properties and been expected to apply to various industrial utilizations. The size of bubble is so small that the nanobubble can be existed in the solution without floatation. Also the internal pressure of bubble is considered to be very large, a large amount of guest molecules is expected to exist in the area of dissociation although the bubble is too small to be observed by an optical microscope. In the present study, we aim to confirm the existence of nanobubbles in the solution after the gas hydrate dissolution. We used the transmission electron microscope to observe the nanobubbles by using the freeze-fracture replica technique.

Keywords: nanobubble, gas hydrate, memory effect, freeze-fracture replica technique, transmission electron microscope

TEM observation of dissolution process of sodium chlorate nanocrystals

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Recent years, we are focusing on nanometer scale live imaging of nucleation and dissolution of crystals in a solution using transmission electron microscope (TEM) to know the fundamental processes. Since, basically, high-vacuum environment has to be maintained in the TEM during the observation, sample is limited. To overcome the difficulties to introduce a solution into a TEM, very ingenious graphene cell or specially designed amorphous silicon nitride membrane has been established and achieved in situ observation of nucleation [e.g., 1-4]. As the results, several new perspectives such as, non-classical nucleation pathway, coalescence and oriented attachment, in the nucleation process have been reported. Against the use of liquid cell, we used ionic liquid as a solvent instead of water to avoid evaporation of a solvent in the high-vacuum of a TEM [5]. Ionic liquids have a great properties for TEM observation, such as negligible vapor pressure and high electrical conductivity. As the result, following new consequences were found after experiments of sodium chlorate nanocrystals.

1. Solubility-independent formation of polymorph.
2. Crystals do not dissolve smoothly but in a fluctuating manner.
3. New crystals form even in a totally dissolving system.
4. Ripening occurs but different from Ostwald ripening.

In case of Ostwald ripening, initially presenting larger particles grow as a result of dissolution of smaller particles. However, our observation shows that ripening occurs with accompanying formation of new crystals, i.e., most of the initial crystals is replaced by new crystals. In the presentation, we will show the difference of the dissolution process between in ionic liquid and water solutions, which can be observed by a special holder having a liquid cell for TEM observation.

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Keywords: TEM, dissolution, nano, in-situ observation

Dissolution behavior of compacted smectite clay

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Smectite, a clay mineral forming natural bentonite widely exists in altered meteorite to sedimentary rock as micro to nano-crystal. Since smectite can appear in the various forms from as-grown {001} stacking to random-aggregate, its dissolution behavior is poorly understood. For example, dissolution of colloidal suspension of smectite can be driven by solution pH, undersaturation ΔG and temperature (Sato et al., 2005), while compacted smectite is stabilized (Nakayama et al., 2004).

Among many approaches for dissolution of smectite, AFM (atomic force microscopy) can directly measure dissolving nano-dispersed particles, but high-density random aggregates. In order to improve AFM, we developed in-situ VSI (vertical scanning interferometry) and auto-compaction cell. By this means, we conducted in-situ measurements of compacted smectite (Nanotmorillonite) immersed in 0.3M NaOH at 70 °C. This method can realize real-time measurements of decreasing material volume of smectite under various densities. After measurements, recovered particles were measured by AFM to refine the step-edge surface area.

As the result of AFM-assisted VSI measurements, dissolution rates of compacted smectite vary from $2.9E-11$ mol/m²/s (density 0.001, Sato et al., 2005) to $2.6E-13$ mol/m²/s (density 1.64, compacted, Satoh et al., 2013). Most possible reason explaining this behavior is self-masking effect which nano-particulates mask step-edges each other (reduced dissolution). However, compaction on random aggregates induces edge-dislocation that newly produces dissolution centers. This was well-recognized especially in the early compaction stage (promoted dissolution).

Thus, high density clay as nano-stacked or aggregated particles always accompanies with dissolution, but it is not continued by self-masking effect as a kind of negative-feedback mechanism. To investigate and understand such a complex behavior of clay, computer simulation by Monte-Carlo calculation is needed.

Keywords: smectite, dissolution, compaction, AFM, VSI

Atomic scale in situ observation of cation exchange on montmorillonite surface

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The clay minerals are expected to apply for the assessment of radioactive waste due to their ion exchange property. While the stoichiometry of the ion exchange has been understood well, the dynamics of the ions at the clay-solution interface, such as the effect of topography of the clay surface on selectivity of the ion exchange and the surface diffusion of the ions, has not been clarified.

We performed in situ observation of the ion exchange on the montmorillonite with atomic resolution in the 0.1 ~ 1 M cesium chloride solutions by the frequency modulation atomic force microscopy (FM-AFM). The montmorillonite is 100 nm plate-like crystal whose interlayer cations are sodium and calcium ions. The replacement of the ions on the montmorillonite surface was identified by the change of the configuration of the lattice of the montmorillonite surface in the cesium chloride solutions. We introduce the result of the FM-AFM observations of the atomic-scale change of the montmorillonite surface depending on the concentration of the cesium ions.

Keywords: clay, montmorillonite, ion exchange, frequency modulation AFM

Surface Free Energy of Fluorite and Apatite Crystals

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Specific surface free energy (SSFE) is significant value to explain the morphology of crystal. The relationship between SSFE and growth length of crystal face is considered to be proportional, which is known as Wulff's relationship, and well accepted for thermodynamic interpretation of crystal growth theoretically. Though Wulff's relationship is well accepted for theoretical analysis, experimental measurement of SSFE for crystal face is very few. According to Young's equation, SSFE of solid face can be introduced from contact angle of liquid on the solid face, and we observed SSFE of some crystals, for example, apatite[1], ruby[2], and quartz[3]. However, the SSFEs of crystal face have wide distribution even for a flat face of the crystal. Such wide distribution of observed SSFE was considered to result from steps on the crystal face. In this work, we observed SSFE of natural fluorite crystal. Natural fluorite crystal was cut and polished for (100), (110), and (111) faces. SSFE can be separated to dispersion component which results from van der Waals force and polar components which results from interaction between permanent dipole moments. The polar component of SSFEs on (100) and (111) faces were smaller than have large rate of dispersion component of than that on (110) face, because (100) and (111) faces are polarized face. Although the SSFE of real crystal is calculated from macroscopic value such as contact angles of liquid droplets, the SSFE reflects microscopic surface structure such as steps and the ionic morphology of the crystal face. We also observed SSFEs of apatite and fluorite crystals in order to demonstrate the effect of steps on the SSFE. Contact angle of water and formamide droplet on crystal face was observed using digital camera. SSFE was calculated using Fowkes approximation and Wu's harmonic mean equations. Though the crystals we experimentally obtained were growth form, the relationship between SSFE and the growth rate was almost proportional, which looks to satisfy Wulff's relationship qualitatively.

Keywords: Surface free energy, apatite, fluorite

Numerical simulation of step dynamics: Quantitative formulation based on a phase-field method

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Step dynamics on a crystal surface is one of the fundamental processes of crystal growth. Growth units such as atoms and molecules in the ambient phase are incorporated into kink sites at the step front, and the step then spreads along the crystal surface, resulting in the growth of the crystal in the vertical direction (layer-by-layer growth mechanism). Therefore, the physics of supply and advancement of steps should be clarified for understanding the crystal growth mechanism.

In 1949 a spiral growth mechanism was proposed to explain non-negligible growth of crystals at low supersaturation [1]. If a screw dislocation emerges normally at the crystal surface, it acts as an eternal step source and forms a spiral hillock with the dislocation outcrop as the top. The normal growth rate is given by an analytic formula as a function of supersaturation [2,3]. A formula giving the hillock slope versus supersaturation plus the measurement of the slope as a function of supersaturation allows us to determine the free surface energy of the step riser and the Burgers vector of the step sources [4,5]. However, these analytic formulas do not describe the dynamics of individual steps. Actual growing crystal surface shows complex step behaviors, for example, emergence of a closed-loop step between two dislocations with opposite signs, and formation of new step islands due to two-dimensional nucleation [6]. In order to investigate the effect of the complex step behaviors on the crystal growth, an alternative method that can treat the dynamics of numerous steps simultaneously is required.

In this study, we proposed a new numerical scheme to calculate the dynamics of numerous steps quantitatively based on a phase-field (PF) method. The PF method has been developed as a numerical technique for simulating the step dynamics on crystal surface [7]. In this method, two-dimensional height profile on the crystal surface is expressed by an order parameter termed *phase*, which takes a constant value between steps (terrace) and bridges between two different-height terraces continuously within a finite width. We newly defined a free energy functional including a supersaturation term explicitly and derived a governing equation for the phase field (PF equation) based on the minimum free energy principle. We also formulated the PF equation so that the advancing rate of a straight step corresponds to that determined by the direct integration hypothesis (exact solution) [3] at a small supersaturation limit. We applied this scheme to some step dynamics problems to check the validity. We confirmed that the advancing rate of a straight step could be calculated accurately with optimized computational parameters. We examined the growth and dissolution of a two-dimensional island in supersaturation condition and found that the time evolution of its radius agrees with the analytic solution including the Gibbs-Thomson effect. We also introduced screw dislocations according to [7] to calculate the normal growth rate of the spiral growth mechanism. Our numerical results agreed with the analytic formulas [2,3] in various cases: a single dislocation, a pair of dislocations with opposite/like signs, and an array of dislocations with equal interval.

Note that our simple formulation requires only a single parabolic partial differential equation to be solved numerically. Our scheme would provide a new approach for the study of crystal growth.

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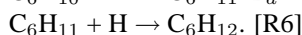
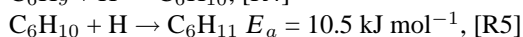
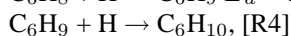
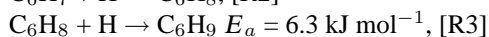
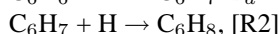
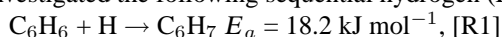
Keywords: Crystal growth, Step dynamics, Numerical simulation, Phase field method

Controlling surface tunneling reactions of solid benzene via surface structure

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Organic molecular solids including thin films and fine particles generally exhibit a range of crystalline phases as well as an amorphous state. The dependence of chemical reactivities on their surface structure has attracted considerable attention because they play a crucial role in an almost limitless amount of research fields, ranging from atmospheric and interstellar chemistry to biological and material sciences. However, despite the rapid accumulation of structural information about organic materials, the correlation between the surface structure of these materials and their chemical properties is not fully understood. Here, we demonstrate that the surface structure of an organic molecular solid determines its chemical reactivity toward an adsorbate. We investigated the following sequential hydrogen (H) atom addition to amorphous and crystalline benzene (C₆H₆)



E_a is the activation barrier for H-atom addition in the gas phase. The radical recombination reactions R2, R4, and R6 are barrierless on the surface. In situ infrared spectroscopy revealed that cold H atoms can add to the amorphous benzene surface at 20 K to form cyclohexane (C₆H₁₂) by tunneling. However, hydrogenation of crystalline benzene is greatly suppressed. We suggest that the origin of the high selectivity of hydrogenation by tunneling is the difference of geometric constraints; that is, the presence of reactive dangling C₆H₆ molecules that lacks near neighbors on the amorphous C₆H₆ surface and the strong intermolecular steric hindrance on the crystalline C₆H₆. The present findings can lead us to a better understanding of heterogeneous reaction systems involving tunneling, and also provide the possibility of nonenergetic surface chemical modification without undesired side reactions or physical processes.

Keywords: Aromatic hydrocarbons, hydrogenation, amorphous structure, crystalline structure, quantum tunneling, reaction control

Large molecular dynamics simulations of the vapor-to-liquid nucleation of water

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Phase transitions play important roles in many areas of science and technology. The classical nucleation theory (CNT) is the most widely used model for describing homogeneous nucleation and provides the nucleation rate as a function of the supersaturation ratio and the surface tension of a condensed phase. However, many studies have reported that the CNT fails to describe experimentally obtained results. In the case of water, the deviations between the nucleation rates predicted by the classical nucleation theory and the experimental values are several order of magnitude.

Molecular dynamics (MD) simulations are able to directly resolve details of the nucleation process, and provide useful test cases for nucleation models. Until now, many MD simulations examining the nucleation process of water molecules have been carried out [1-3]. Tanaka et al. [3] performed MD simulations of the nucleation of water vapor in order to test nucleation theories with 4000 water molecules. The results showed that the classical nucleation theory (CNT) and the modified classical nucleation theory (MCNT) overestimate the nucleation rates in all cases. On the other hand, the semi-phenomenological model, which corrects the CNT prediction using the second virial coefficient of a vapor, reproduced the formation free energy of a cluster within 10% and the nucleation rate J within one order of magnitude. The sticking probability of the vapor molecules to the clusters was also determined from the growth rates of the clusters. The sticking probability rapidly increases with the supersaturation ratio S , which is similar to the Lennard-Jones system. For such low- S cases, we must estimate the sticking probability precisely for the evaluation of J .

Previous typical MD simulations of homogeneous nucleation use 10^3 - 10^4 atoms. At low vapor densities, and therefore low supersaturations, a single nucleation event becomes unlikely to occur within reasonable computational timeframes. Simulations with larger number of molecules allow for the occurrence of such rare nucleation events, and enable us to measure these low rates. Recently, we started the large-scale MD simulations the SPC/E rigid water model with LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). In the simulations, the particle numbers are 1 to 120 million atoms (324000-4116000 molecules). We assumed NVT (constant volume and temperature) ensembles and used a three-dimensional periodic boundary condition with different parameters of temperature T and initial supersaturation ratio S . Here, first results for the large-scale simulations are presented. We obtained the smaller nucleation rates by 4-5 order of magnitude than the previous studies.

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Keywords: nucleation, vapor to liquid transition, molecular dynamics simulation, water

Homogeneous Nucleation of Nanoparticles from Supersaturated Vapor Investigated by In-situ IR Measurement Experiment

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When we evaporate experimental materials in the atmosphere, nanoparticles condense from highly supersaturated vapor via homogeneous nucleation. This technique is known as the Gas Evaporation method. Nuclei must overcome energetic disadvantage of surface by making chemical bonds to form particles. Since energetic barrier for homogeneous nucleation is excessively high, homogeneous nucleation occurs from highly supersaturated vapor [1-3]. In such conditions, precursors should grow following kinetically feasible reaction path, which is deviated from equilibrium condensation. Furthermore, the size of nuclei is so small that they show quite different physical and chemical properties from that of bulk material. Therefore, chemical reaction processes and its properties during transition state of homogenous nucleation are still unrevealed.

For the purpose of examination of condensation sequences of nanoparticles, we investigated by a new experimental apparatus named Free-flying *In-situ* infrared measurement of Nucleating nanoparticles Experimental (FINE) system [4]. FINE system is for gas evaporation method combined with FT-IR and enables direct *in-situ* IR measurement of condensation of 10-100 nm nanoparticles via homogeneous nucleation from vapor.

We applied FINE system for silicate and titanium oxides and revealed that condensation proceeds through metastable phases with non-crystalline IR feature, which is known as Ostwald's step rule. Just condensed nanoparticles would be liquid droplet and crystallization proceeded subsequently. In previous study, we succeed in measurement of IR evolution after nucleation. However, the information about precursors is still lack to understand condensation mechanism. We are now developing a new experimental set up for FINE system and going to talk about future work.

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Keywords: Homogeneous Nucleation, Vapor Growth, in-situ, Nanoparticles

Application of the transmission electron microscopy to the study of the crystallization process in a solution

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One of the powerful methods to demonstrate the crystal growth and dissolution processes is in situ observation using a microscope, because it can directly visualize these processes in real time. The crystal growth and dissolution processes in a solution have been studied mainly using various optical microscopies as a noninvasive technique. Some high resolution optical microscopies is able to visualize the molecular-level structure on a crystal surface [1-3]. However, the lateral resolution of optical microscopy is sub-micron because it is limited by the wavelength of a light source [1]. To resolve the crystallization processes more clearly, the transmission electron microscopy (TEM), which has the nano-order resolution, is a strong method for in situ observation. Recently, in situ observations of the crystallization processes in solutions under TEM have been energetically performed using the liquid cells or an ionic liquid to adapt to the high-vacuum environment [4-6]. These observations allow us to see the behavior of nano-particles and crystallization process of inorganic materials in a solution. Here, using the liquid cell, we have performed in situ observation of the crystallization of a lysozyme protein, which is used to study the crystallization process in a solution as a model material, by the TEM for understanding the processes of crystallization.

We used two TEMs with LaB6 filament at an acceleration voltage of 200 kV (Hitachi H-8100) and with field-emission gun at an acceleration voltage of 300 kV (Hitachi HF-3300). For the observation of crystals in a solution, we used a "Poseidon" TEM holder (Protochip, Inc.) combined with a liquid cell. The liquid cell consists of a pair of semiconductor-based plates with an amorphous silicon nitride window and 150 or 500-nm-thick spacer to form the flow path of the crystallization solution. The lysozyme was crystallized using NaCl as a precipitant in a sodium acetate buffer solution at pH = 4.5.

As a result, we succeeded in observing the crystals and amorphous particles of lysozyme protein using the TEM and the liquid cell holder. In this presentation, we report the recent results of in situ observation of its crystallization process including the growth and dissolution.

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Keywords: in situ observation, transmission electron microscopy, crystallization, solution growth, lysozyme

Growth and dissolution of the hydrogel-grown lysozyme crystals

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We recently developed a new method for growing protein crystals in a high-concentration hydrogel. Using the method we can crystallize protein crystals with increased mechanical stability, as a result the crystals give us high resolution of X-ray diffraction pattern. On the other hand the crystals contain the hydrogel fragments and the effects on crystal defects such as dislocations were unknown. In this study, we slightly etched the crystal surface and estimated the dislocation density.

Hydrogel-grown and solution-grown LZM crystals were slightly dissolved by increasing the temperature, and their surface morphologies were observed by laser confocal microscopy. The solution-grown crystals exhibited deep etch pits at 303 K, while the hydrogel-grown crystals exhibited etch pits at a higher temperature (305 K). In addition, the density of the etch pits on the solution-grown crystals at 305 K was significantly higher than that on the hydrogel-grown crystals at the same temperature. These results demonstrate that the hydrogel-grown crystals are more tolerant of temperature changes than those grown in solution.