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 encaged 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