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Nanobubble nucleation studied using Fresnel fringes in liquid cell electron microscopy

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ABSTRACT

Liquid cell electron microscopy is a useful technique for the observation of chemical, biological, and mechanical processes in liquids at nanometer-scale resolution. This study investigated the generation and growth of nanobubbles using the Fresnel fringe method, which enabled us to determine the location of bubble interface; the nanobubbles were induced in the 600-nm-thick water sample in the cell, by the electron beam. Nucleation occurred first at the solid–liquid interface in the upstream side of electron beam, and this was followed by second-group nucleation at the downstream-side interface; all of the stable nucleations occurred on the solid surfaces. The size of the nucleated bubbles at the moment they became visible depended on the magnification used in the electron microscope, and a higher-energy density in the electron beam induced larger bubbles. The underlying mechanism was also considered in this study.

1. Introduction

Micro/nano-scale bubbles have recently attracted much attention, because of their remarkable advantages for a wide range of applications, from aquaculture [1] to microelectronic surface-cleaning [2,3]. Nanobubbles are expected to show higher performance than microbubbles, but the mechanisms responsible for their generation and behavior remain unclear. For example, an air bubble with a diameter of 100 nm is theoretically predicted to collapse in 100 μs, or shorter, because of the high Laplace pressure [4,5], but recent experimental studies have confirmed lifetimes longer than several hours for such bubbles, using atomic force microscopy [6,7]. Nanobubbles can be categorized into bulk and interfacial nanobubbles; the former type exists in the bulk liquid [8,9], and the latter type stays at solid–liquid interfaces [6,7,10–18]. An understanding of the generation and stability of interfacial nanobubbles is the key to understanding the initial stage of bubble nucleation, which occurs, for example, at the onset of nucleate boiling (ONB) in pool boiling. However, the nucleation mechanism remains unclear, despite the fact that many researchers over many years have dedicated their efforts to understanding and controlling phase change phenomena [19–23]. In the literature [24] nucleation is treated using idealized thermodynamics, or an entrapped gas phase is modeled as the starting point of nucleation. However, bulk-based theories cannot correctly analyze the interactions between solid atoms and liquid molecules, and consequently our knowledge of the mechanism responsible for vapor generation near the heated surface is lacking. The main reason why the real phenomena of nucleation have not been pinned down is the difficulty of in-situ observations, which is due to the small size of nucleation (i.e., smaller than 1 μm). Thus, in order to break through the current technological barrier of boiling heat transfer, a new experimental technique enabling the investigation of the dynamic behavior of nanobubbles near the solid–liquid interface is highly desirable.

Recently, a nano liquid cell fabricated using MEMS technology was reported to enable the observation of the generation and growth of interfacial nanobubbles using transmission electron microscopy (TEM) or scanning transmission electron microscopy (STEM) [25–31]. This technique is called liquid cell electron microscopy (LCEM) [32–37]; LCEM enables the direct observation of samples in their native condition, and is useful to explore biochemical "wet" processes at a nanometer-scale spatial resolution [38]. The phase change produced by a microheater [26] has also been investigated using LCEM; the heating pulse induced the rapid expansion of vapor bubbles, but no great understanding of nucleation on scales smaller than 100 nm was achieved. It is known that most of the bubble generation in water-based LCEM results from

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radiolysis due to the electron beam–water interactions[28], but the fundamental behaviors of nanobubbles are identical regardless of the produced species, which gives valuable information on nucleation near a solid surface. However, there is very limited data regarding bubble generation in the sub-100-nm range, and previous experiments have reported only the horizontal position of nanobubbles, because the liquid thickness is typically made as thin as possible, in order to achieve high resolution. For example, by employing a graphene cell [30] a very high spatial resolution in the encapsulated gas phase was achieved. The coalescing process and the Ostwald-ripening process have been observed in an ultra-thin water film, at the approximately-10 nm scale [30]; however, in this study we sought to understand the behavior of nanobubbles in a liquid sample thicker than 100 nm, and it was therefore necessary to measure their vertical position. In this paper, we make the first report of three-dimensional pictures of multiple bubble nucleation in the sub-100-nm range, deduced from TEM images; this was achieved by developing a new method based on the Fresnel diffraction of an electron beam. This method will contribute to the further development of LCEM, and to the efficient control of nucleate boiling in the future.

2. Material and methods

A nano liquid cell was prepared as shown in Fig. 1, using a commercially available chip (Structure Probe. Inc., West Chester, PA, USA) of a 3.0 mm × 3.0 mm × 200 μm Si (100) substrate with an Si_3N_4 window. The thickness, length, and width of the window were 50 nm, 500 μm, and 500 μm, respectively. Two microchips were stacked face-to-face with each Si_3N_4 window. There was a gap between the Si_3N_4 windows. Pure water transferred into the gap with the help the capillary phenomenon and was confined using epoxy resin, not to leak into the ultrahigh vacuum in the TEM. An epoxy resin layer functioned as a spacer, and the windows were made parallel. The gap was measured using laser microscopy (VK-9710, KEYENCE) under atmospheric pressure, and was estimated to be 600–650 nm, both at the center and near the edge of the window. However, it should be noted that when the sample was placed in the TEM, the window bulged, due to the pressure difference [39]. The water was thicker than the pre-measured thickness in our TEM experiments. However, our TEM observations were conducted at a point near the edge of the window, because the focus of the electron beam was confirmed at the edge. The water thickness at this observed point was greater than, but not notably different from, that measured at atmospheric pressure.

The nano liquid cell was imaged using a TEM (JEM-3200FSK, JEOL Ltd., Tokyo, Japan) operated at 300 kV, using an emission beam current of 108 μA. Images of the irradiation area were recorded using a CCD camera operated at 10 fps. The magnification could be controlled from 5×10^3 to 4×10^5, and the vertical position of the observation point was shifted manually.

Liquid cells often contain air bubbles between the windows [28,31]. If a large bubble is present, an ultra-thin water film can remain on the windows and this film may contain voids [31] that look like bubbles. We checked and confirmed that there were no air bubbles between the windows, before and after the TEM experiments [34].

3. Results

When the TEM electron beam was operated at magnifications from 2×10^5 to 4×10^5, hazy and bright regions appeared, the

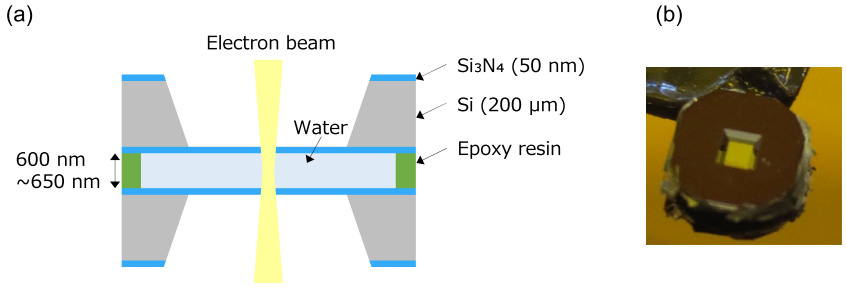

Fig. 1. Nano liquid cell. (a) Schematic illustration of a nano liquid cell. A thin layer of pure water was sandwiched between two Si_3N_4 membranes and sealed in using epoxy resin, which prevented the water from evaporating in the vacuum. (b) Image of a fabricated nano liquid cell.

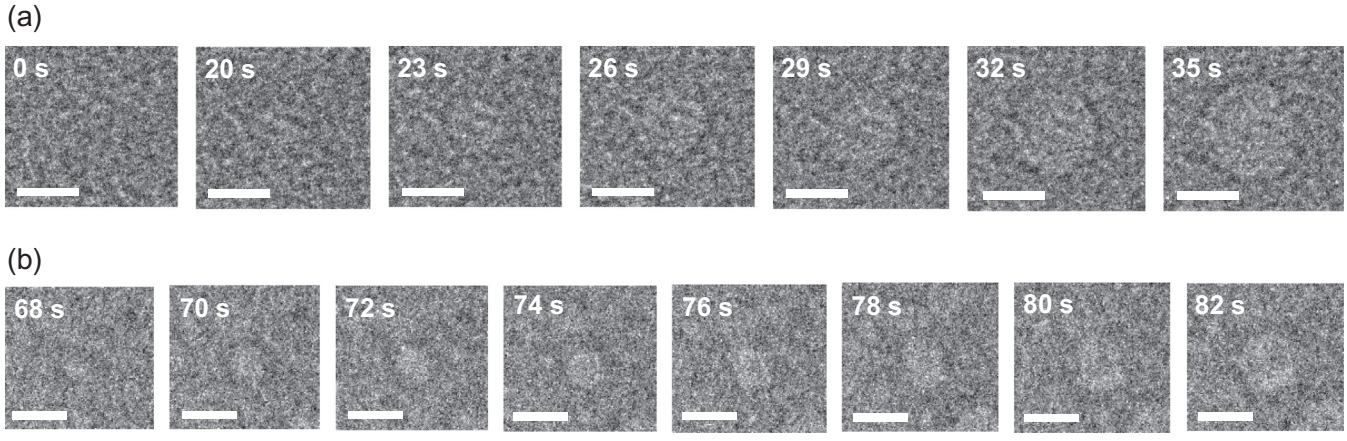

Fig. 2. Images illustrating the generation of the gas phase and transformation into nanobubbles during TEM observations. (a) TEM images of water at a magnification of 3×10^5. 23 s after TEM electron beam irradiation was started, an embryonic gas phase was formed, and subsequently transformed into a nanobubble. (b) TEM observations were performed using a magnification of 2×10^5. It took 70 s of irradiation time for bubble nucleation to occur. The scale bars in all images are 10 nm.