Ultramicroscopy 180 (2017) 188–196

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Perspectives on in situ electron microscopy

Haimei Zheng[a,b,*], Yimei Zhu[c,d]

[a] Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
[b] Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA
[c] Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, NY 11973, USA
[d] Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY 11790, USA

ARTICLE INFO

Article history:
Received 8 November 2016
Revised 12 March 2017
Accepted 18 March 2017
Available online 29 March 2017

Keywords:
In situ TEM
Liquid cell TEM
Aberration correction
Colloidal nanocrystal growth
Ferroelectric vortices
Ferromagnetic domains switching

ABSTRACT

In situ transmission electron microscopy (TEM) with the ability to reveal materials dynamic processes with high spatial and temporal resolution has attracted significant interest. The recent advances in in situ methods, including liquid and gas sample environment, pump-probe ultrafast microscopy, nanomechanics and ferroelectric domain switching the aberration corrected electron optics as well as fast electron detector has opened new opportunities to extend the impact of in situ TEM in broad areas of research ranging from materials science to chemistry, physics and biology. In this article, we highlight the development of liquid environment electron microscopy and its applications in the study of colloidal nanoparticle growth, electrochemical processes and others; in situ study of topological vortices in ferroelectric and ferromagnetic materials. At the end, perspectives of future in situ TEM are provided.

1. Introduction

In situ electron microscopy has been identified as one of the major future directions of electron microscopy (BES workshop report [1]). It provides the opportunity to observe at the atomic level materials responses to an external stimulus, discover transient states during chemical or structural transformations, and correlate materials structure to their functionalities [2–5]. There are many fascinating research topics using in situ transmission electron microscopy (TEM) owing to the advances of in situ methods, ranging from liquid and gas environment TEM [3,4] to pump-probe ultrafast microscopy [6-8], nanomechanics [9,10] and ferroelectric domain switching [11,12]. With the advances in electron microscopy, it has been possible to achieve 0.5 Å spatial resolution using an aberration corrected TEM [13], high speed data acquisition (~2.5 ms or better) with a fast camera [14] and electron energy loss spectroscopy (EELS) enables the study of spin waves with an energy resolution down 1 or 2 meV [15]. Many of these advances can be attributed to the earlier critical contribution from Dr. Ondrej Krivanek [16-18]. For in situ measurements, it is often a challenge to achieve the best performance of an aberration corrected microscope due to an unideal thick sample, sample vibration in chemical reactions or under an external stimulus, insufficient electron flux during fast data acquisition and so on. However, it is clear that with the advances in electron microscopy including the aberration corrected TEM, EDS with large collection angle, fast and sensitive electron detection, large data processing, in situ electron microscopy has become increasingly powerful and popular. There is no doubt in situ TEM will bring significant impact in broad areas of research from materials science to physics, chemistry and biology.

In this article, a few recent in situ TEM work in the area of *materials chemistry*, such as colloidal nanoparticle growth and electrochemical processes using liquid environmental cells, and in *solid state physics*, such as topological vortices in ferroelectric and ferromagnetic materials, ferroelectric or ferromagnetic domain switching are highlighted. We hope this article can help to provide a view on the broad applications of in situ TEM. At the end, conclusion and an outlook into future challenges and opportunities in in situ TEM including the impact of aberration corrected TEM and fast electron detection are provided.

The development of liquid cells has opened many opportunities for the study of materials dynamic processes in liquids with TEM, such as, nucleation and growth, self-assembly of nanomaterials, electrochemical processes, biological materials in physiological conditions, etc. In the past a few years, publications on the topic of liquid cell TEM study have increased rapidly [4]. Here, we review a few recent studies on nanoparticle growth in a liquid cell with atomic resolution imaging and high temporal resolution (400 frames per second), the in situ lithiation/delithation of MoS_2 nanoflakes in an electrochemical cell with EDS and nanobeam

* Corresponding author.
E-mail addresses: hmzheng@lbl.gov, zhu@bnl.gov (H. Zheng).

http://dx.doi.org/10.1016/j.ultramic.2017.03.022
0304-3991/

diffraction, which highlight the growing impact of in situ liquid environmental electron microscopy in materials chemistry and chemical research.

In the second part of this paper, a couple of examples on in situ electron microscopy of ferroelectric or ferromagnetic vortexes and domain switching are provided. There has been significant recent interest on topological phase transitions and topological phases of matter. Topological structures, emerging near spontaneous symmetry-breaking transitions, are ubiquitously observed in wide branches of science [19-22]. In condensed matter, topological defects can be promising candidates for information storage technology. Skyrmions, multiferroic vortices, domain walls, dislocations, and disclinations are examples, where emergent properties and behaviors have been reported [23-28]. These topological defects are invariant under continuous deformations or perturbations, and thus said to be protected by topology. They often are observable and play important roles in phase transition. Their fascinating underlying physics responsible for striking geometric patterns can be found in order parameter space [29]. In situ TEM is a unique approach to topological structures, where the aberration corrected electron microscopy plays a major role.

2. In situ TEM study of materials dynamics in liquids

Most liquids including water and other organic solvent have a high vapor pressure, thus they are incompatible with the high vacuum environment of a transmission electron microscope. To separate the liquid samples from the vacuum environment, a sealed liquid cell is required. A liquid cell needs a thin imaging window allowing electron beam to go through while being able to survive in high vacuum. The concept of windowed TEM cell was introduced in the early days of electron microscopy. From the earliest attempt of imaging wet samples using sandwiched thin aluminum foils in 1930s [30] to the liquid cells nowadays with thin SiNx/Si membrane [31,32] or graphene liquid cell [33] or electrochemical cells allowing an applied electric bias [34], tremendous progress has been made and breakthrough discoveries have been achieved.

The self-contained liquid cells with ultra-thin SiNx membrane (as thin as 10 nm [32]) or graphene offer superb atomic image resolution [33]. SiNx membranes are mechanically strong, inert, with low imaging contrast thus excellent for electrochemical cells. Various types of patterned electrodes (e.g., Au, Ti, Al, Pt, graphene, etc.) can be made into an electrochemical liquid cell with SiNx membranes. It is also possible to flow liquids between the two silicon nitride membranes of a liquid cell using external tubing and a syringe pump, which has been widely used in a commercial liquid cell stage and is attractive for the study of reactions with instant mixing of liquids.

Liquid cell TEM has been used for the exploration of new frontiers for materials synthesis, electrochemistry, catalysis, fluid physics, biological materials in aqueous environments and many other areas of research [3]. Compared to many other in situ approaches, such as in situ optical spectroscopy, [35] x-ray spectroscopic methods, [36-40] atomic force microscopy (AFM) and scanning tunneling microscopy (STM), [41-43] in situ TEM has its unique advantages allowing directly observation of materials transformation dynamics in liquids with high spatial down to the atomic range and high temporal resolution in millisecond. The major criticisms come from the electron beam radiation damage and the challenges in controlling of local environment, reactant mixing, etc. during reactions, which will also be discussed in this article.

2.1. Liquid cell TEM study of colloidal nanocrystal growth

Crystallization process in colloidal solution is complex involving the arrangement of thousands of atoms and molecules near the surface, and it is further complicated by the interactions between atoms and the environment changes [44]. With modifications of the temperature, precursor and surfactants, it is possible to make various nanocrystals with certain size and shape, on which there have been many studies [45,46]. Liquid cell TEM is a unique method to study nanocrystal growth mechanisms by revealing single nanoparticle trajectories and elucidating the role of different factors in controlling structure and morphology of a nanoparticle [4].

Here, we show a series of successful studies on nanoparticle shape evolution to highlight the significant progress that has been made on liquid cell TEM owing to the liquid cell development and the advances in electron microscopy and fast electron detection. For example, in colloidal nanocrystal synthesis, it is often assumed that in order to achieve monodisperse nanoparticles coalescence between nanoparticles should be avoided. It was reported by Zheng et al. [47] that with real time liquid cell TEM, observations reveal two types of growth, either by monomer attachment or by coalescence, leading to the same particle size (Fig. 1a) [47]. Fascinating growth by nanoparticle attachment has also been observed in Pt-Fe nanowire formation [14]. The interactions between Pt-Fe nanoparticles result in nanoparticle end-to-end attachment into a chain (Fig. 1b). Further systematic liquid cell TEM studies by changing the surfactant concentration have been carried out and the results have demonstrated that surfactants can drastically influence morphology of a nanoparticle, modify the growth rate of certain facets, inhibit nanoparticle aggregation, and prevent coalescence [44].

Another example is on in situ high resolution imaging of Pt nanocrystal growth and shape evolution with liquid cell TEM [32]. Wulff construction [48,49] has been used to predict the equilibrium shape of nanocrystals, where it states that the growth rate of certain facet is proportional to the surface free energy. For the growth of nanocrystals the high-energy facet grows at a higher rate than the low-energy facets, therefore, the fast growing facets will eventually disappear resulting in a nanocrystal terminated with low energy facets [50,51]. It was assumed that the commonly used surfactants modify the energy of specific facets through preferential adsorption, influencing the relative growth rate of different facets thus the shape of a nanocrystal [52,53]. However, in situ observations of Pt nanocube formation using liquid cell TEM show drastic deviation from the Wulff construction prediction [32]. As shown in Fig. 1c and d, we found the growth rates of all low index facets, {1 0 0}, {1 1 0} and {1 1 1}, are similar until the {1 0 0} facets stop growing. The {1 1 0} facets will continue to grow until they reach a limit, at which point they form an edge of a nanocube. The continued growth of {1 1 1} facets fills the corners of the cube. Such atomic facet development in platinum nanocube growth suggests the surface energy minimization rules breaks down at the nanoscale. Density functional theory (DFT) calculation reveals that the drastic differences of ligands mobility on different facets, i.e., ligands move several orders of magnitude slower on {1 0 0} than {1 1 1} facets retarded the growth of {1 0 0} facets. Therefore, a selective facet arrested shape control mechanisms is proposed. The improved liquid cells with thinner SiNx membranes and a fast electron detector with high detection quantum efficiency (Gatan K2 IS camera) are critical for achieving high spatial resolution at the atomic level.

In addition, graphene liquid cells with reduced background noise offer unprecedented resolution (Fig. 2). Park et al. used an aberration-corrected TEM and direct electron detector to resolve the growth and 3D atomic structures of Pt nanocrystals in a graphene liquid cell [33,54]. The observation revealed that Pt nanoparticle coalescence is site-selective and the {1 1 1} facets with lowest surface energy or lowest ligand coverage are preferred for nanoparticle attachment [54].