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Atomic resolution imaging of *in situ* InAs nanowire dissolution at elevated temperature

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Abstract. We present a preliminary study of the *in situ* heating of InAs nanowires in a gaseous environment in an environmental transmission electron microscope. Nanowire dissolution, accompanied by dynamic reshaping of crystalline Au-containing catalyst particles at the ends of the wires, is observed, accompanied by indium oxide crystallite formation nearby.

1. Introduction

Catalytic growth of semiconductor nanowires is of considerable interest [1], but is poorly understood at the atomic level. Some nanowires can be grown below the eutectic temperature of the catalyst-semiconductor alloy, leading to the proposal of a vapor-solid-solid growth mechanism [2]. Here, we examine InAs nanowires, whose growth by chemical vapor deposition is known to drop abruptly above ~500 ºC [3]. We image nanowires just above this temperature in the transmission electron microscope (TEM) in a gaseous environment, as a preliminary experiment aimed at understanding the behavior and imaging properties of semiconductor nanowires in an environmental TEM, in advance of attempting true *in situ* III-V nanowire growth. We observe a complex dynamic nanowire dissolution process accompanied by subsidiary crystallite formation.

2. Experimental Details

InAs nanowires containing InP barriers were grown by chemical beam epitaxy at 390ºC. A bright-field TEM image showing a selection of nanowires, which are each capped by a Au catalyst particle and supported on a C film for TEM imaging, is shown in Fig. 1. The nanowires were examined at 300 kV in an image-aberration-corrected FEI Titan 80-300 TEM equipped with a differentially-pumped environmental cell. Motivated by recent reports that the surfaces of similar nanowires can be cleaned using atomic hydrogen [4], the nanowires were examined at elevated temperature in a H_2 atmosphere.

3. Results

The InAs nanowires were heated to 520 ºC in 1.3 mbar H_2 *in situ* in the TEM. Unexpectedly, under these conditions, the Au-containing particles changed shape dynamically while remaining crystalline, as confirmed by the presence of lattice fringes in the image shown in Fig. 2. Dissolution of the wires proceeded, apparently at the catalyst-nanowire interface, with the wires shrinking in length. New crystallites were observed to form on the support film adjacent to the nanowires.

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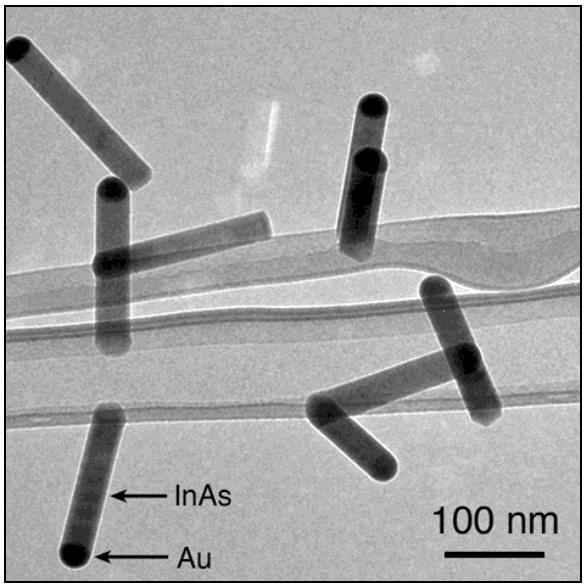

Fig. 1. Bright-field image of nanowires imaged at room temperature.

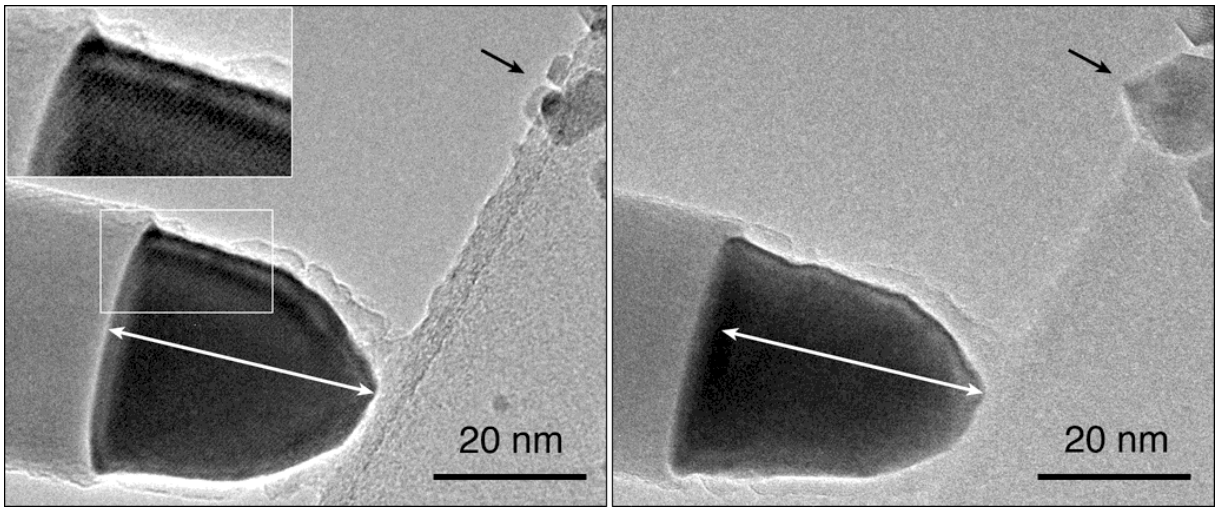

Fig. 2. Images acquired 3 minutes apart at 520 ºC in 1.3 mbar H_2, showing lattice fringes in a Au-containing particle at the end of an InAs nanowire. The white arrows, which have the same length, illustrate the elongation of the catalyst particle. New crystallites form close to the wire at the position indicated by the black arrow.

Fig. 3 shows three snapshots taken from a movie illustrating dynamic changes in the shape of a crystalline Au-containing particle during dissolution of an InAs nanowire. The brighter region in the wire is a segment of InP. Dissolution of the InP segment is observed to proceed faster than that of the InAs. Crystallites are observed to form in the upper-right corner of each frame. Lattice fringe contrast in both the particle and the nanowire is visible in Fig. 4, which shows the presence of a ledge at the interface during nanowire dissolution. Fig. 5 shows high-resolution lattice images acquired both during and after crystallite formation, as well as an electron energy-loss spectrum, confirming that the crystallites are In_2O_3. Neither As nor P were detected in the crystallites. The original thin amorphous coating on the nanowire surface, which is visible in Figs 2 and 3, remained as a product next to the Au particle. This coating was subsequently identified using electron energy-loss spectroscopy as being composed primarily of C.

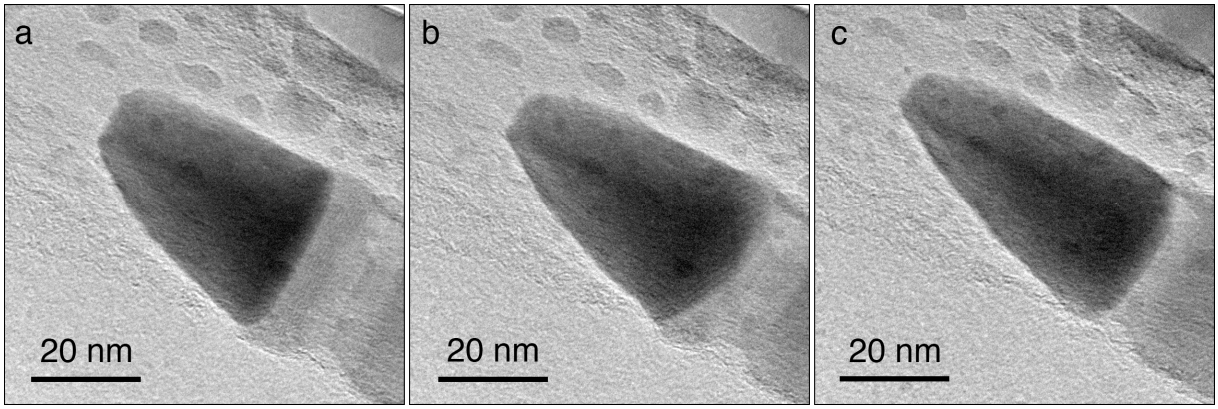

Fig. 3. Three frames, separated by 7 seconds, taken from a movie of InAs nanowire dissolution. A short segment of InP is visible as a lighter-contrast segment of the wire.

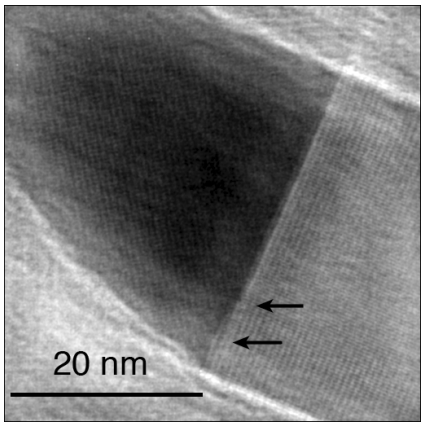

Fig. 4. One Fourier-filtered frame taken from a movie acquired during InAs nanowire dissolution. Lattice fringe contrast is visible both in the Au-containing particle and in the InAs nanowire, indicating that they are both crystalline at this temperature (520 ºC). The image also confirms that lattice fringe contrast can be observed in the presence of 1.3 mbar of H_2 in the differentially pumped section of the electron microscope column. Ledges are visible at the particle-nanowire interface (arrowed).

4. Discussion

The crystalline nature of the Au-containing particle at the temperature used in the present experiments, which is above the growth temperature of the InAs nanowires, suggests that the particle may also have been crystalline during nanowire growth at lower temperature. The interaction between the Au-containing particle and the support film may play a role in the observed shape changes. The formation of In_2O_3 crystallites is surprising as there is no intentional source of oxygen in the microscope. Some native oxide on the nanowire is likely, but residual gas in the environmental cell is a more likely source given the amount required for particle formation. The present observations illustrate the complexity of even a nominally straightforward heating experiment carried out in an environmental TEM. Parameters that may affect the observed dissolution process include specimen temperature, gas environment, the interaction between the Au particle and the carbon support film and the effect of the incident electron beam both on the specimen and on the surrounding gas.

5. Conclusions

Preliminary results from *in situ* heating of InAs nanowires in H_2 in an environmental TEM reveal, at atomic resolution, a complicated nanowire dissolution process, which appears to proceed at the nanowire-catalyst interface. During this process, the Au-containing catalyst particle remains crystalline but changes shape dynamically. At the same time, In_2O_3 crystallites form adjacent to the wire. All aspects of such a simplified experiment should ideally be understood before proceeding to the additional complication of introducing reactive gases to grow III-V nanowires *in situ* in the TEM.

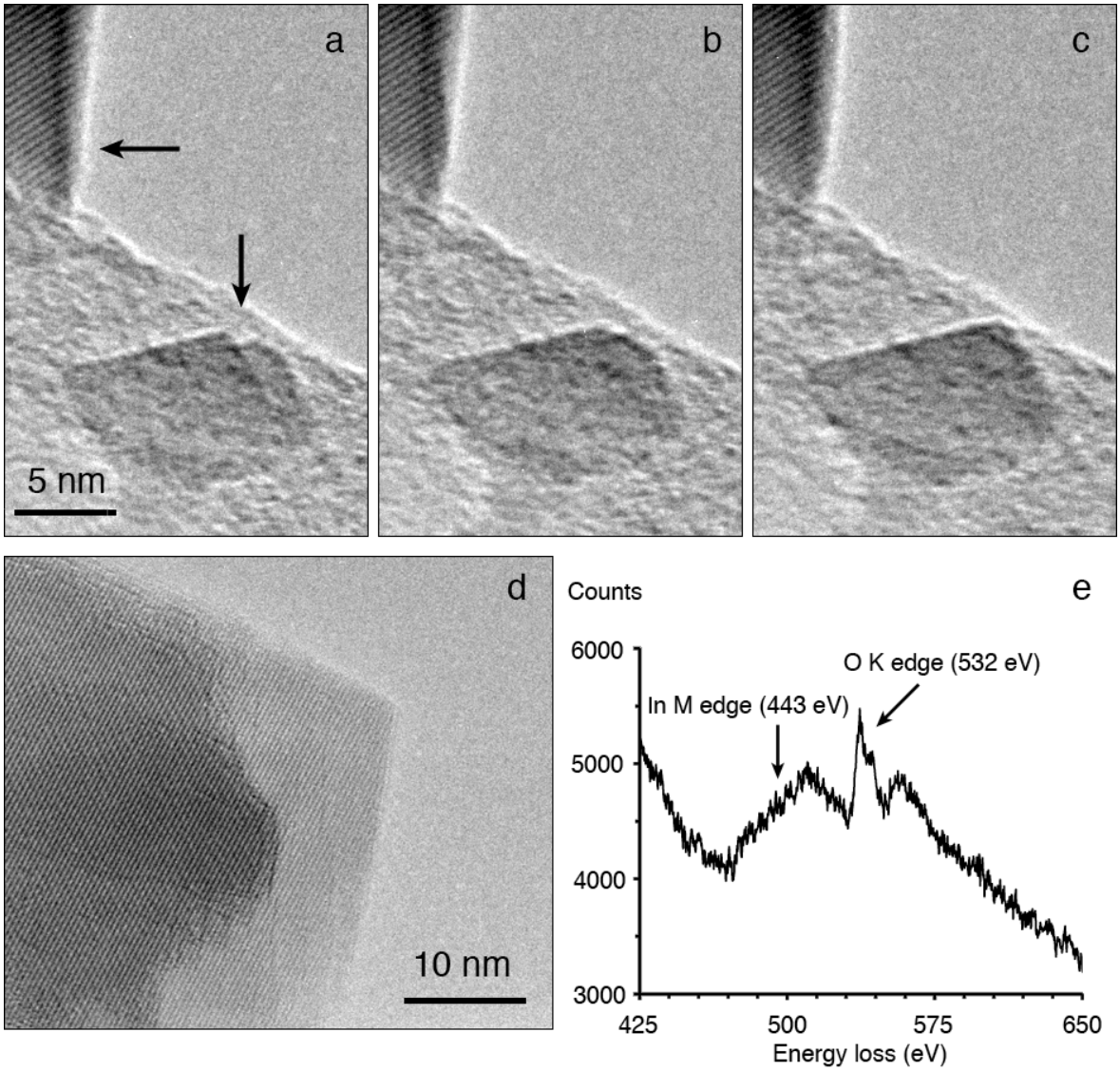

Fig. 5. a) - c) High-resolution lattice images showing crystallite formation adjacent to a nanowire. d) High-resolution lattice image and e) electron energy-loss spectrum acquired from crystallites after nanowire dissolution, with In and O peak edges indicated [5], confirming the formation of In_2O_3.

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