Published in final edited form as:

Micron. 2013 ; 0: 82–86. doi:10.1016/j.micron.2013.07.009.

Determination of the surface morphology of gold-decahedra nanoparticles using an off-axis electron holography dual-lens imaging system

J. Cantu-Valle^a, F. Ruiz-Zepeda^a, E. Voelkl^b, M. Kawasaki^c, U. Santiago^a, M. José-Yacamán^a, and A. Ponce^{a,*}

^aDepartment of Physics and Astronomy, University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249, USA

^bHolowerk, LLC, Austin, TX 78732, USA

^cJEOL USA, Inc., 11 Dearborn Road, Peabody, MA 01960, USA

Abstract

The purpose of this paper is to show surface irregularities in gold decahedra nanoparticles extracted by using off-axis electron holography in a JEOL ARM 200F microscope. Electron holography has been used in a dual-lens system within the objective lenses: main objective lens and objective minilens. Parameters such as biprism voltage, fringe spacing (σ), fringe width (W) and optimum fringe contrast have been calibrated. The reliability of the transmission electron microscope performance with these parameters was carried out through a plug-in in the Digital-Micrograph software, which considers the mean inner potential within the particle leading a precise determination of the morphological surface of decahedral nanoparticles obtained from the reconstructed unwrapped phase and image processing. We have also shown that electron holography has the capability to extract information from nanoparticle shape that is currently impossible to obtain with any other electron microscopy technique.

Keywords

Electron holography; Dual-lens system; Transmission electron microscopy; Metallic nanoparticles

1. Introduction

It is well known that theoretically fivefold symmetry metal nanoparticles such as decahedral or icosahedral are predicted not to be stable beyond a size of around 2 nm (Barnard et al., 2009). Experimentally it has been shown conventional methods of synthesis of decahedral nanoparticles beyond that size and until about 200 nm. Evidence of stability has been found in decahedral nanoparticles of about 200 nm called typically Marks decahedron in which notches and wedges stabilize to the nanoparticles (Marks, 1994). There is a very strong possibility that further defects will appear at larger sizes that will facilitate the growth of

*Corresponding author. Tel.: +1 210 458 5474. arturo.ponce-pedraza@utsa.edu, arturo.ponce@utsa.edu (A. Ponce).

these nanoparticles. Unfortunately, conventional TEM provides very limited information on the third dimension. In principle dark field techniques can give information as shown by Yacaman and Ocaña (1977); however, the technique is limited by the extinction distance values which are limited to 10 nm at best. In contrast, electron holography offers a unique way to study the third dimension of nanoparticles with a better height resolution (~1 nm). This detection limit is in the same order of magnitude as the lattice constants of noble metals and entails to a better probing of the surface defects such as steps. This will open a better understanding of the growth of nanoparticles.

In this work we show surface discontinuities with nanometric steps distributed at the surface and interfaces of the decahedron, which are not directly observable by other electron microscopy techniques such as high-angle annular dark field (HAADF) microscopy or high resolution transmission electron microscopy (HRTEM). As is known, image formation in a HR-TEM consists of an incident plane wave often coming from the highly-coherent field emission electron source that interacts with the sample. The wave that exits the specimen, the object exit wave, contains key physical information about the sample, but during the image acquisition process the intensity I of the image is recorded as square of the amplitude of the wave, while the phase and thus substantial information from the sample is lost $I = |\psi|^2$. The phase lost during the image recording process contains critical contributions such as: the phase modulation of the crystal and additional electrostatic and magnetostatic external fields, optical phase modulation due to distortion from the digital camera (charge-coupled device, CCD), from lattice distortion and projector lens (Hytch et al., 2011).

In transmission electron microscopy there are common ways to estimate the electron-transparent thickness of the studied specimens such as electron energy loss spectroscopy (EELS) and diffraction contrast imaging. A less common method is electron holography in which the thickness of the sample is directly related to the phase shift of the object wave when the mean inner potential (MIP) of the material is given (Lichte and Lehmann, 2008; Tonomura, 1999). In addition, morphology and the shape of individual nanoparticles can be extracted from holograms. Particularly for polyhedral nanoparticles there is no TEM-related technique capable of extracting the 3D shape from a single projected image while providing surface information of the nanoparticles. For metallic nanoparticles, we consider in the holograms the contribution of the mean inner potential within the nanoparticle, as given by the zero-order Fourier coefficient (V_0) (Spence, 1993). In the reconstructed phases, an unwrap phase process should be applied in order to avoid a $\pm 2\pi n$ thickness jump of the phases, this process has been developed in the current work using HoloWorks v5.0.4 (Volkl et al., 1995).

In addition, we report the off-axis electron holography using the flexible dual-lens system in a JEOL ARM 200F for the first time. The described method allows for a simplified, reproducible and calibrated setup. In our case we chose a field of view (FOV) between 250 and 300 nm. Other FOVs can be chosen just as easily and reproducibly for the characterization of materials in nanotechnology for extracting quantitative information such as electrostatic fields (Ortolani et al., 2011; Zhang et al., 1992; McCartney et al., 1997, 2010), magnetic fields (Hirayama et al., 1995; Osakabe et al., 1983), non-stained biological samples (Simon et al., 2004, 2008), and impurities in solids, determination of the thickness

and the lattice distortion in nanostructured materials and dopant profiles and strain measurement in semiconductor technology (Cooper et al., 2011; Muehle et al., 2005; Hytch et al., 2011).

2. Experimental

An electron hologram is a fringe-modulated image containing the complete information, amplitude and phase, of an electron transparent object. The holograms are formed by the interference between one reference and one object wave, due to a biased electron biprism. (schematically shown in Fig. 1). After the acquisition, the hologram is numerically reconstructed into a complex image, from where it is possible to extract both the amplitude and the phase image.

A typical TEM setup for off-axis electron holography can be thought of as consisting of three parts, an illumination system, an imaging system, and a projection system (Wang et al., 2004). For the JEOL JEM-ARM 200F, the illumination system consists of three condenser lenses C1, C2, and minilens (CM). The imaging system consists of two objective lenses: the main objective lens (OL) and objective minilens (OM) coupled with an electron biprism manufactured by JEOL, Ltd. that is placed near the first image plane of the selected area aperture. The electron biprism comprises of a filament and two electrodes and located on the opposite sides of the filament, which is exited by a DC voltage applied to the filament. The biprism is made of a thin wire of platinum having a diameter of about 0.4–0.5 μm . Below the imaging system, there is a projection system, formed with 3 Intermediate lenses and a projector lens, which normally provide the proper image size for the recording media. The images can be recorded by selecting one of two different CCD cameras: the Gatan UltraScan camera or the GIF (Gatan imaging filter) Tridiem camera. The microscope was operated at non-standard lens excitation, with C1 maximized and CM set to zero in order to optimize the coherence of the beam. Also, the first intermediate lens is set to zero. Under these circumstances the projection system does no longer provide enough magnification and for this reason we take advantage of the GIF camera that provides an additional 10 $\times$ magnification.

The dual-lens imaging system allows a variable magnification with respect to the projection system providing a wide range of field-of-view (FOV). The imaging operation consists of a virtual image formed by the objective lens (OL) and a real image formed in a fixed imaging plane by the objective minilens (OM) as shown in Fig. 2. (a) Fringe width, fringe spacing and fringe contrast were determined by the equation reported by (Wang et al., 2004). By continuously altering the two objective lenses, the magnification of the object can be changed while the interference pattern remains almost unchanged with respect to the CCD camera. Under these circumstances, the fringe contrast remains fairly stable as well.

For the gold decahedra nanoparticle we set the magnification using 5.5 V in the OL. In order to select the appropriate parameters, the fringe spacing and interference fringe width was measured for different biprism excitations, shown in Fig. 2(a). In Fig. 2(b) the FOV was filled by the interference fringes by applying 20 V in the biprism obtaining a FOV of 275 nm. Fringe spacing is obtained from an intensity line profile in Fig. 2(c). Holograms were

reconstructed with $\sigma = 1.3$ nm for a spatial resolution of 3.9 nm (Lichte, 2007) and a fringe contrast of 37%. Higher fringe contrast and number of electrons in the holograms, imply better signal to noise ratio in the reconstructed phase and amplitude images (Völkl et al., 1995; Voelkl and Tang, 2010).

3. Results

After the reconstruction, both phase and unwrapped phase images were obtained (Fig. 3(a) and (b)). The oriented particle shows a smooth contour from the center to the edge of the nanoparticle and no abrupt phase shift was observed. In Fig. 3(b) the phase image was calibrated using the mean inner potential of the FCC Au. Taking the background as reference the thickness profile can be computed, and a thickness computation line profile is shown in Fig. 3(d). The phase image (Fig. 3(c)) has been amplified $2.5\times$ and the routine employed can reach a phase resolution value of $2\pi/1000$ (Voelkl and Tang, 2010).

A phase shift of $\phi = 2\pi$ due to a specific thickness (τ) can be calculated using $\phi = C_E|V_0|\tau$, where V_0 represents the mean inner potential for the FCC Au (25 V) we are aware that the mean inner potential can vary depending, e.g., on the angle of the illumination with respect to the zone axis of the crystal (Tonomura, 1987). These changes however would not affect the conclusions in this paper and are therefore suppressed for simplicity, and C_E for the 200 kV accelerating voltage is 0.00729 rad/V nm. We obtained a phase shift of $\phi = 2\pi/30$. Therefore this is the minimum detectable phase difference needed to solve steps of 1.2 nm. For a monatomic surface step ($2.35 \text{ \AA}$), the required phase resolution is from the order of $\pi/100$, the routine employed can reach a phase resolution value of $2\pi/1000$ (Voelkl and Tang, 2010) which is more than what we need to detect the morphological irregularities presented.

The surface topology of the image was analyzed in a Matlab code (showed in Fig. 4). One important feature extracted from the unwrapped phase has been the irregularities of the surface, clearly observed in Fig. 4. In this image, a 3D surface reconstruction is shown. These irregularities show superficial information not achievable with conventional TEM or HAADF images of the nanoparticle oriented in the same zone axis. This has important consequences on the physics of nanoparticles and its applications.

In order to obtain a systematic model of the reconstructed phase, we used a geometrical model escalated to respect the symmetry and growing of the decahedron analyzed. In this way, Fig. 5 shows schematically the superposition of a perfect structure and the shape obtained by the phase reconstructed from the hologram (taken from the surface obtained in the topography of Fig. 4) to delimit the contour of the surface.

4. Discussion

We have generated a model of the decahedron using a geometrical code based on Matlab. The irregularities observed in the reconstructed decahedron were matched to this model and are shown in Fig. 6. We have generated a continuous model by creating a 3D mesh in *.obj* file format based in the coordinates matrix values of unwrapped phase image and we have manipulated them using MeshLab. MeshLab is an open source, portable and extensible

system for the processing and editing of 3D structures. Considering a bi-pyramidal symmetry, we created a mirror image with respect to the xy plane of the image.

The model shown in Fig. 6 shows that the nanoparticle has steps, wedges in the corners and complicated rough surface is consistent with a structure produced by the kinetics as recently discussed by (Patala et al., 2013). The steps with kinks correspond to the morphology obtained by growth by step movement, i.e., atoms are added to the steps which provoke their movement, which is a classical mechanism for crystal growth. In addition, we can observe the growth of two dimensional isolated islands on the surface and the formation of wedges along the twin boundaries which are consistent with previous reports (Barnard et al., 2009). The growth of a nanoparticle can be the result of equilibrium and then a minimum energy shape structure is produced or the result of growth kinetics that can result in a complicated shape. The many steps in the decahedral structure in Fig. 6 indicate a growth by advancing steps. Due to that additional atoms are being incorporated to the nanoparticle during growth new layers are created subsequently.

5. Conclusion

The capabilities of this holographic technique in a JEOL ARM 200F microscope lead to the precise determination of the morphological surface of decahedral nanoparticles obtained from the unwrapped phase reconstructed and image processing. We have also shown that electron holography has a resolution that allows the study of nanoparticle shape with unprecedented resolution. This opens up a very power tool for nanostructure analysis.

Acknowledgments

This project was supported by grants from the National Center for Research Resources (5 G12RR013646-12) and the National Institute on Minority Health and Health Disparities (G12MD007591) from the National Institutes of Health. The authors would like to acknowledge to the NSF for support with grants DMR-1103730, “Alloys at the Nanoscale: The Case of Nanoparticles Second Phase and PREM: NSF PREM Grant # DMR 0934218. Also would like to acknowledge to CONACYT – 311149 and the Instituto de Innovación y Transferencia de Tecnológica de Nuevo León I²T².

References

- Barnard AS, Young NP, Kirkland AI, van Huis MA, Xu H. Nanogold: a quantitative phase map. *ACS Nano*. 2009; 3(6):1431–1436. [PubMed: 19489558]
- Cooper D, Béch A, Hartmann JM, Hutin L, Le Royer C, Rouviere JL. Strain measurement for the semiconductor industry with nm-scale resolution by dark field electron holography and nanobeam electron diffraction. *Journal of Physics: Conference Series*. 2011; 326:012025.
- Hirayama T, Tanji T, Tonomura A. Direct visualization of electromagnetic microfields by interference of three electron waves. *Applied Physics Letters*. 1995; 67(9):1185.
- Hytch MJ, Houdellier F, Snoeck E. Dark-field electron holography for the measurement of geometric phase. *Ultramicroscopy*. 2011; 111(8):1328–1337. [PubMed: 21864773]
- Lichte H. Performance limits of electron holography. *Ultramicroscopy*. 2007; 108:256–262. [PubMed: 18053649]
- Lichte H, Lehmann M. Electron holography – basics and applications. *Reports on Progress in Physics*. 2008; 71:46.
- Marks LD. Experimental studies of small particle structures. *Reports on Progress in Physics*. 1994; 57:603–649.

- McCartney MR, Agarwal N, Chung S, Cullen DA, Han MG, He K, Li L, Wang H, Zhou L, Smith DJ. Quantitative phase imaging of nanoscale electrostatic and magnetic fields using off-axis electron holography. *Ultramicroscopy*. 2010; 110(5):375–382.
- McCartney MR, Smith DJ, Farrow RF, Marks RF. Off-axis electron holography of epitaxial FePt films. *Journal of Applied Physics*. 1997; 82(5):2461.
- Muehle U, Lenk A, Weiland R, Lichte H. Characterization of dopants distribution using electron holography and FIB-based lift-off preparation. *Microelectronics Reliability*. 2005; 45(9–11):1558–1561.
- Ortolani L, Houdellier F, Monthieux M, Snoeck E, Morandi V. Surface electrostatic potentials in carbon nanotubes and graphene membranes investigated with electron holography. *Carbon*. 2011; 49(4):1423–1429.
- Osakabe N, Yoshida K, Horiuchi Y, Matsuda T, Tanabe H, Okuwaki T, Endo J, Fujiwara H, Tonomura A. Observation of recorded magnetization pattern by electron holography. *Applied Physics Letters*. 1983; 42(8):746.
- Patala S, Marks LD, Olvera de la Cruz M. Elastic strain energy effects in faceted decahedral nanoparticles. *Journal of Physical Chemistry C*. 2013; 114:1485–1494.
- Simon P, Lichte H, Formanek P, Lehmann M, Huhle R, Carrillo-Cabrera W, Harscher A, Ehrlich H. Electron holography of biological samples. *Micron*. 2008; 39(3):229–256. [PubMed: 17374487]
- Simon P, Lichte H, Wahl R, Mertig M, Pompe W. Electron holography of non-stained bacterial surface layer proteins. *Biochimica et Biophysica Acta*. 2004; 1663(1–2):178–187. [PubMed: 15157620]
- Spence JCH. On the accurate measurement of structure-factor amplitudes and phases by electron diffraction. *Advances in Chromatography*. 1993; A49:231–260.
- Tonomura, A. *Electron Holography*. Springer; 1999. p. 162
- Tonomura A. Applications of electron holography. *Reviews of Modern Physics*. 1987; 59(3):639–669.
- Voelkl E, Tang D. Approaching routine $2\pi/1000$ phase resolution for off-axis type holography. *Ultramicroscopy*. 2010; 110(5):447–459.
- Völkl E, Allard LF, Frost B. A software package for the processing and reconstruction of electron holograms. *Journal of Microscopy*. 1995; 180:39–50.
- Wang YY, Kawasaki M, Bruley J, Gribelyuk M, Domenicucci A, Gaudiello J. Off-axis electron holography with a dual-lens imaging system and its usefulness in 2-D potential mapping of semiconductor devices? *Ultramicroscopy*. 2004; 101(2–4):63–72. [PubMed: 15450653]
- Yacamán MJ, Ocaña T. High-resolution dark-field electron microscopy of small metal particles. *Phys Status Solidi A*. 1977; 42:571–577.
- Zhang X, Hashimoto T, Joy DC. Electron holographic study of ferroelectric domain walls. *Applied Physics Letters*. 1992; 60(6):784 9.

Fig. 1.
Off-axis electron holography ray diagram.

Fig. 2.

(a) Fringe spacing and interference fringe width versus biprism voltage. (b) Reference image taken at a biprism voltage of 20 V and 5.5 V in OL and (c) intensity line profile versus fringe spacing σ (nm).

Fig. 3. Au decahedral nanoparticle: (a) Phase reconstructed image, (b) unwrapped phase image, (c) 2.5 $\times$ amplify-phase lines processed and (d) computed thickness obtained using the Au crystalline potential.

Fig. 4.
Surface plot in a pseudo-isometric representation of the phase reconstructed in the gold decahedral nanoparticle.

Fig. 5.

(a) Overlapping data of the holographic and the perfect model, (b) model adjusted by the contour of the reconstructed phase and (c) surface obtained after the superposition with the reconstructed phase surface.

Fig. 6.
(a) Reconstructed phase meshed and (b) geometrical continuum model.