Electric radiation mapping of silver/zinc oxide nanoantennas by using electron holography

J. E. Sanchez,¹ F. Mendoza-Santoyo,^{1,a)} J. Cantu-Valle,¹ J. Velazquez-Salazar,¹ M. José Yacamán,¹ F. J. González,² R. Diaz de Leon,³ and A. Ponce¹

¹Department of Physics and Astronomy, University of Texas at San Antonio, San Antonio 78249, USA

²Coordinación para la Innovación y la Aplicación de la Ciencia y la Tecnología, Universidad Autónoma de San Luis Potosí, San Luis Potosí 78210, Mexico

³Instituto Tecnológico de San Luis Potosí, San Luis Potosí 78437, Mexico

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In this work, we report the fabrication of self-assembled zinc oxide nanorods grown on pentagonal faces of silver nanowires by using microwaves irradiation. The nanostructures resemble a hierarchical nanoantenna and were used to study the far and near field electrical metal-semiconductor behavior from the electrical radiation pattern resulting from the phase map reconstruction obtained using off-axis electron holography. As a comparison, we use electric numerical approximations methods for a finite number of ZnO nanorods on the Ag nanowires and show that the electric radiation intensities maps match closely the experimental results obtained with electron holography. The time evolution of the radiation pattern as generated from the nanostructure was recorded under *in-situ* radio frequency signal stimulation, in which the generated electrical source amplitude and frequency were varied from 0 to 5 V and from 1 to 10 MHz, respectively. The phase maps obtained from electron holography show the change in the distribution of the electric radiation pattern for individual nanoantennas. The mapping of this electrical behavior is of the utmost importance to gain a complete understanding for the metal-semiconductor (Ag/ZnO) heterojunction that will help to show the mechanism through which these receiving/transmitting structures behave at nanoscale level. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4906102>]

I. INTRODUCTION

Intermetallics-semiconductor nanostructures have developed are promising active elements that emulate a metallic nanostructure, which will act as a transmission line "electrically" connected to a semiconductor material that can be used as building blocks for nanoantennas.^{1–4} Moreover, the frequency response for these systems is known to be useful in the design of nanoantennas, solar cells, optoelectronic detectors, and nonlinear optical devices.^{5–7} In particular, zinc oxide (ZnO) has become one of the most promissory semiconductor materials to be used in metal-semiconductor alloys due to the fact that its structure and morphological arrangements can be controlled in a precise way to match a particular metal-semiconductor configuration. The combination of a metal with ZnO has demonstrated interesting physic-electrical properties that could be manipulated when acting in a particular optoelectronic application.^{8–10} Furthermore, it has been reported that using different ensemble mechanisms for the metal-semiconductor structure, it is possible to integrate highly ordered silver-zinc oxide (Ag/ZnO) nanostructure systems.⁸ It is worth pointing out here that most of the ZnO nanostructure production methods are based on chemical reactions involving synthesis and thermal treatments at high temperatures (around 400–500 °C) with reactions times around 48 h.¹¹ Despite the fact that these methods lead to well aligned nanostructures, normally in a

preferential c-axis direction and with high stability, it is well known that they are time consuming with high production costs a major drawback in profitable market industries, where mass production has to be considered. An alternative chemical synthesis process is the microwave irradiation process (MIP), which has demonstrated a significant time reduction compared with the thermal chemical synthesis methods.^{11–14} Besides, the MIP method also stimulates the growth with precise control and distribution of well-aligned crystalline nanostructures. One of the most important characteristics in this growing process for Ag/ZnO systems is the control of their morphological distribution that is associated to their electrical properties observed due to the metal-semiconductor junction. In order to theoretically study the influence of the geometrical arrangement on the electrical properties in a variety of similar systems, several approaches on numerical electromagnetic code techniques are used to understand the electrical and its time evolution response in this type of high order nanostructures.^{15,16} An experimental approach worth noticing uses specific optical techniques that allow the mapping of the electrical response of metal-semiconductor junctions. Specifically, using near field optical microscopy as well as Fourier microphotoluminescence measurements, it is possible to scan the near and far electric fields using polarized light that induces a charge distribution on the metal-semiconductor junction, enabling to study the electric near/far field behavior.^{17–19}

Today's available literature contains many reports on fundamental theory related to furthering the understanding

^{a)}On sabbatical leave Centro de Investigaciones en Óptica, León, Guanajuato 37150, Mexico.

of the metal-semiconductor electric behavior. Nonetheless, the experimental corroboration for these theoretical models is limited on the subject of nanoantennas reception/transmission mapping of their near and far electric field, particularly during their excitation by means of an external electrical radio frequency (RF) signal. Hence, this paper presents the research on a new chemical reaction based on the MIP method to assemble ZnO nanorods on silver nanowires in a hierarchical nanostructure configuration resembling a nano-antenna. We also report on a novel method that applies an *in-situ* modulated RF signal to map these nanoantennas' electric field at nano-scale level using off-axis electron holography.

II. EXPERIMENTAL DETAILS

A. Nanoantenna fabrication

The Ag/ZnO metal-semiconductor system has been synthesized by establishing a two step process. First, silver nanowires were fabricated by following the polyol method: 5 ml of ethylene glycol (EG) were heated at 160 °C for 40 min; next, a silver nitrate AgNO₃ (reagent grade 99.99% by Sigma-Aldrich) is reduced in a solution of EG following the addition of polyvinyl pyrrolidone (PVP, Mw 55,000 reagent grade 99.99% by Sigma-Aldrich); (EG) and (PVP) act as reducer solution and capping agent to polar molecules, respectively; the mixture is subjected to a constant stirring rate for a period time, 40 to 60 min, until the silver nanowires reach the desired and most stable diameter (~70 nm) and length (more than 2 μm), as described in Refs. 20 and 21. Separated images of these silver nanowires have been

included in the supplementary material (Fig. S1). As for the second part, during the self- assembling process of ZnO nanorods on silver nanowires (Ag-NWs), we established an innovative method to reproduce a metal-semiconductor (Ag/ZnO) heterojunctions, as follows: Zinc acetate dihydrate (Zn(Ac)₂, 98% reagent by Sigma-Aldrich), 5–25 mM and hexamethylenetetramine (HMT) 5–25 mM were dissolved in deionized water to form a precursor initial solution; next, 200 μl of silver nanowires, as obtained by the polyol method, were added to the former solution, which is now irradiated using an ETHOS EZ Microwave Digestion System, working within 400 to 700 W at a microwave frequency of 2.5 GHz; Figures 1(a) and 1(b) show a schematic representation of the MIP process just described. The vial containing the precursor solution (Fig. 1(a)) is heated between 20 °C–90 °C, with an exposure reaction time from 1 to 50 min; the thermal ramp for the microwave process is shown in Fig. 1(b), as a function of the reaction time. The second column in Fig. 1(c) reveals the time dependent morphological features on Ag/ZnO system.

B. Morphological and chemical characterization

The Ag/ZnO nanoantennas were characterized by using scanning electron microscopy (SEM) with a field emission gun FEG-SEM Hitachi S5500 DF/BF detector operated at 30 kV at an emission current of 20 μA. In the micrographs, Figs. 2(a) and 2(b), it is observed ZnO nanorods growing well aligned in a multi-pentagonal distribution along the faces of the silver nanowires (010) planes, as corroborated by x-ray diffraction. In addition, the length average for ZnO

FIG. 1. A schematic representation of the microwave irradiation process at different reaction times. (a) The vial containing the precursor solution is irradiated with microwaves between 400 and 700 W at 2.5 GHz. (b) shows the thermal ramp followed as a function of time for the different stages; x varies from 1 to 20 min to obtain the most stable nanostructure. (c) Variation of the epitaxial distribution of ZnO nanorods along the silver nanowires at different reaction times, it was observed an increasing about 7 to 27 in the linear density distribution ρ (number of ZnO_{rods}/silver length) of the nanorods as listed.

FIG. 2. SEM images of ZnO/Ag hierarchical nanoantennas. (a) shows a low magnification view of the ZnO/Ag nanoantennas as grown by the MIP process; (b) the high-resolution image details the distribution of ZnO rods along the silver nanowire; (c) shows the structure models of the pentagonal cross section view and the ZnO nanorods distribution; and (d) an experimental cross section view showing the epitaxial growth of ZnO on (100) planes on the silver nanowires. The bar scale in the SEM images corresponds to 1 μm .

nanorods was determined to be 0.8 μm along the (0001) growth axis (Fig. 2(b)). In fact, the well-defined 3D pentarrangement of ZnO rods creates a metal-semiconductor junction with Ag nanowires serving as support for the ZnO nanorods mimicking an electrical transmission line, where the whole Ag/ZnO nanostructure actually resembles an aerial antenna (Fig. 2(c)). Here, it should be noticed the precise control in the morphology and distribution of the ZnO nanorods forming the (Ag/ZnO) system through controlling the time in the MIP process. The number of ZnO rods per silver wire length (hereafter called ρ) was controlled and determined by observation to be 25 to 30 rods/ μm . It was also inferred that the synthesis reaction process that produces the most stable configuration of Ag/ZnO nanoantennas is given by the reaction time of 20 min as shown in Fig. 1(c). In fact, a cross section view of Ag/ZnO nanoantennas (Fig. 2(d)) shows the distribution of ZnO nanorods assembled themselves in a pentapolar configuration. The angle was measured between ZnO nanorods to be about 72°, which matches with the internal angles of a geometrical pentagon, an indication of the epitaxial growth of the Ag/ZnO nanostructures.

The chemical analysis was obtained in a map elemental composition by x-ray energy dispersive spectroscopy (EDS) using a Bruker x-ray silicon drift detector (SDD) into the FEG-SEM Hitachi S5500. Individual mapping for each element of the Ag/ZnO nanoantennas has been recorded separately. In Fig. 3(a), a secondary electrons (SE) micrograph shows the region, where the chemical analysis was performed. Figures 3(b) and 3(c) show the distribution of the zinc and oxygen composition along the ZnO nanorods, represented by a pseudo-color map in green and red, respectively. It is also observed the compositional EDS analysis of the silver nanowire (inclined magenta line in Fig. 3(d)), and as expected acting as the core of the nanoantenna system with ZnO nanorods grown perpendicular to the silver wire. Finally, all elements are mapped in a combined pseudo-color map (Fig. 3(e)).

III. RESULTS AND DISCUSSION

In order to understand the electrical properties surrounding the metal-semiconductor nanomaterials (ZnO/Ag nanoantennas), electron holography has positioned as a well-established interferometry method in transmission electron microscopy. It is capable to reconstruct the electron-beam paths that go through a sample, thus carrying important information about electrical and magnetic properties within and around it.²² It uses two images, the reference and object holograms, which upon combination on a Charge Couple Device sensor (CCD camera: Gatan Ultrascan 2K $\times$ 2K) produce an interferogram containing the amplitude and phase information related with different physical and mechanical parameters of the sample, in this particular case, its electromagnetic properties. The intensity at the sensor is given by²²

$$I_{\text{Holo}} = I_1 + I_2 + \sqrt{I_1 I_2} \cos(2R_x + \phi_{\text{obj}} + I_{\text{inel}}), \quad (1)$$

where I_1 and I_2 are the reference and object beam intensities, respectively. R_x corresponds to the wave phase number shift, ϕ_{obj} represents a phase term that describes the position of the fringe pattern with respect to camera, and I_{inel} corresponds to negligible electron inelastic processes that do not contribute to the holographic phase reconstruction mechanism. The last term of the sum in Eq. (1) is known the fringe modulation, whose argument gives the information associated with the contribution of the time-space dependent electron beam path related with physical and mechanical parameters such as the electric and magnetic field distributions. The phase reconstruction process is done using the Holoworks v5 script^{23,24} that combine the reference and object holograms in any particular state of the sample. A second pair of reference and object holograms is acquired at another sample state and subtracted from the previous hologram pair, thus rendering a phase map from which it is possible to visualize and measure the sample's electric and magnetic contribution. The phase extraction

FIG. 3. The chemical analysis map by EDX for a Ag/ZnO nanoantenna. (a) SEM high magnification image showing a well defined distribution of ZnO nanorods on silver wires; (b) the EDX analysis shows the distribution of Zinc along ZnO nanorods; (c) oxygen signal; (d) silver signal corresponding to the silver core wire; and (e) reveals the chemical composition of all elements Zn, O, and Ag.

procedure follows a technique that involves a Fourier transformation of Eq. (1) that separates in the Fourier space the first two terms (called the DC term) from the third modulation term such that this one may be filtered and inverse Fourier transformed to obtain the required phase map. Figure 4(a) shows an electron holography off-axis diagram in the transmission electron microscope. The electrical diagram is included in Fig. 4(b), where the chip is shown connected to the sample holder (shield wire). The circuit loop surrounds the nanoantennas transferring the modulated RF signal produced by the synthesized function generator (Fig. 4(b)). A picture of the experimental setup is shown in Fig. S3 in the supplementary material. The sample is positioned in a holey carbon copper grid, the grid is oriented in the plane of the circuit from which the external signal will be received and extracted.

Figure 5(a) shows an image of the reference and object electron beam overlapping, while Fig. 5(b) shows the wrapped phase obtained from the subtraction of two reference-object pairs. The amplitude and phase images are shown unwrapped, i.e., a continuous phase map, in Fig. 5(c). The phase in the unwrapped images allows us to infer a multidirectional intensity distribution associated with the electrical radiation pattern as predicted by numerical electromagnetic codes. As a point of comparison, the radiation pattern was calculated using a numerical electromagnetic code freeware package,¹⁶ for a Yagi-Uda type nanoantenna using the same experimental sample orientation, i.e., so the unwrapped phase is matched. It may be noticed that the simulated radiation pattern has a lower intensity in the center of the antenna, as observed in the azimuthal pattern (Fig. 5(d)) of Fourier plane image of the emitted electromagnetic (EM) waves. The blue and red lines in this figure correspond to the horizontal and vertical EM plane components, respectively. Figure 5(e) shows the EM far field: the qualitative resemblance between the experimentally found electric radiation pattern and the predicted one is quite close.

FIG. 4. The experimental off-axis electron holography setup for the external signal applied to the Ag/ZnO nanoantennas. (a) Depicts the trajectory of the electron beam in a transmission electron microscope. The electron beam wave interacts with the Ag/ZnO nanoantenna excited using the RF signal generator and is combined with a reference wave on CCD sensor. (b) External RF signal applied to the electrical chip where the nanostructures have been placed.

FIG. 5. The directionality of the electric radiation pattern for an isolated Ag/ZnO nanoantenna. (a) Electron hologram of the object (nanoantenna); (b) extracted phase; (c) unwrapped phase and color field bar; (d) Fourier plane image of the emitted EM waves radiation pattern of a simulated Yagi-Uda type nanoantenna, whose orientation is that of the sample; (e) the far field simulated radiation pattern shows a distribution similar to the one obtained in the unwrapped phase (c).

The behavior of the experimental electric radiation map is believed to have been originated by the electron beam induced charge carrier distribution along the surface of the

ZnO nanorods. The electric charge oscillation on the ZnO nanorods has been widely studied in metallic-semiconductor heterojunctions, called an electrical “skin effect.”^{25–27} For

FIG. 6. The time evolution radiation pattern of ZnO/Ag nanoantennas. (a) Cross section view hologram; (b) wrapped phase without excitation; (c) unwrapped phase; (d) unwrapped phase for a frequency increase of 10 MHz at constant amplitude of 5 Vpp; (e) lateral view hologram; (f) wrapped phase without excitation; (g) unwrapped phase; (h) unwrapped phase for an amplitude increase of 5 V at constant frequency of 1 MHz. The lateral inset shows the time evolution for the radiation pattern indicated in the color range bars from low (black) to high (white). (Multimedia view) [URL: <http://dx.doi.org/10.1063/1.4906102.1>] [URL: <http://dx.doi.org/10.1063/1.4906102.2>]

electric radiation time dependent evolution, we have simultaneously applied a sinusoidal EM signal for two nanoantenna orientations, namely, in a cross section view for ZnO nanorods growing along the perpendicular axis-direction to the silver nanowires, Fig. 6(a), and a lateral view, Fig. 6(e). The following conditions were considered: (1) For the cross section, the nanoantenna is stimulated with an EM signal swept in the frequency range 1 to 10 MHz, using steps of 1 MHz per second with constant amplitude of 5 Vpp. The result was recorded and is available in the video S1 found in the supplementary material²⁸; (2) For the lateral view, the amplitude was changed from 0 to 5 V, using steps of 1 V per second at a constant frequency of 1 MHz, refer to video S2 in supplementary material. Videos S1 and S2 show a reconstruction of the electron holograms, the object and reference electron beams (electron hologram), the wrapped and unwrapped phase maps, captured using the Camtasia Studio software.

Figures 6(b) and 6(f) show the EM radiation pattern, where the equally valued phase contours are associated with the varying charge distribution on the Ag nanowire and ZnO nanorods showing a similarity with a reception/transmission aerial structure antenna. Moreover, the back and forth moving charge flow on the nanoantenna produce a propagating electromagnetic wave that may be associated with the changes in the unwrapped phase images Figs. 6(c) and 6(d), where the former has no excitation and the latter has a response to a frequency of 10 MHz with constant amplitude of 5 Vpp. It is possible to observe an increase of the electric field distribution (Fig. 6(d)) when the frequency is increased. For the second condition, Figures 6(g) and 6(h) show unwrapped phase maps with no excitation and excitation using modulated amplitude of 5 Vpp with constant frequency of 1 MHz, respectively. In contrast with the first condition, it may be observed a decrease of the radiation pattern distribution associated with the electrical field surrounding the nanostructure (Fig. 6(h)). Additionally, we performed another numerical simulation showing the pentagonal cross section of a single nanoantenna, included in Fig. S3 of the supplementary material. In agreement with the experimental observation, after the simulation (Figs. 6(c) and 6(d)) a radial distribution pattern is shown.

IV. CONCLUSIONS

Ag/ZnO hierarchical nanoantennas were designed and constructed using an innovative microwave irradiation method. Using electron holography, their surrounding electric field was experimentally mapped and compared with simulations under time evolution for a modulated RF signal applied. It was inferred that the nanoantennas might be capable of transmitting and/or receiving electromagnetic waves when stimulated with a modulated RF signal. The monitoring of the radiation pattern distribution with *in-situ* electron holography TEM contributes technologically toward the applications as active elements (nanoantennas) in radio-responder devices.

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