Enhanced photoemission from nanostructured surface topologies

Ranganath Teki
Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, 110 8th St., Troy, New York 12180-3590

Nikhil Koratkar
Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, 110 8th St., Troy, New York 12180-3590

Tansel Karabacak and Toh-Ming Lu
Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, 110 8th St., Troy, New York 12180-3590

(Received 16 August 2006; accepted 4 October 2006; published online 10 November 2006)

The authors characterized the photoemission behavior of nanostructured surfaces (specifically Ru and Pt nanorod arrays) and observed an ~15-fold enhancement in photocurrent for a slanted Ru nanorod array (nanorods tilted at ~40° to the substrate normal) compared to a planar Ru film. The authors show that the improved performance originates from two basic reasons: (1) increased surface area of the nanorods which enhances the photon-collection probability and (2) single crystal nature of the nanorods which increases electron escape probability due to the absence of grain boundaries. Such nanostructured surfaces show promise in a variety of device applications such as photodetectors, photon counters, and photomultiplier tubes. © 2006 American Institute of Physics. [DOI: 10.1063/1.2387970]

While photoemission has been extensively investigated for planar metal surfaces, the photoemissive response of nanostructured surfaces has not yet been investigated in detail. Our objective in this letter is to systematically study the mechanics of photoemission from nanostructured surfaces such as ruthenium (Ru) nanorod arrays and compare their response with planar Ru surfaces. Our approach for creating the nanostructured surfaces is based on an oblique angle deposition (OAD) technique with substrate rotation. OAD is a physical vapor deposition technique in which flux arrives at a large oblique incidence angle (θ > 70°) from the substrate normal (while the substrate is rotating) as shown schematically in Fig. 1(a). This results in the formation of isolated nanorods [Fig. 1(a)] by the shadowing effect during growth. OAD parameters used for nanorod fabrication are provided in Ref. 12.

A schematic of the photoelectric test setup is shown in Fig. 1(b). The experiments were performed at pressures below ~5 × 10⁻⁶ Torr. A Newport Oriel Xenon 150 W arc lamp was used to shine light on the sample through a sapphire window of 2 in. diameter. The lamp was operated at 145 W. The photocurrent was measured using a Keithley 6487 series picoammeter/voltage source, which was also used to apply a dc voltage between the collector and the sample. The applied voltage was varied from −5 to +10 V. Figure 1(c) shows the current-voltage (I-V) characteristic curve obtained for Ru flat film and Ru nanorod samples with different rod lengths. The saturation photocurrent for the nanorods did not show a strong dependence on the rod length and was ~3.3 times that of the flat film. No filters were used in this experiment, so the light falling on the samples consisted of the entire spectrum of the Xe lamp ranging in wavelength from 200 to 2400 nm. The enhanced photocurrent observed in Fig. 1(c) can arise due to the following reasons: (1) a decrease in the work function for the nanorod samples over the flat film, (2) changes in reflectivity of the nanorod sample compared to the flat film, (3) increased surface area of the nanorods as compared to the planar film, and (4) different crystalline natures of the samples.

We proceeded to analyze each of the above effects in detail. The enhanced photocurrents may originate from a lowering of the work function of the Ru nanorods compared to the planar Ru film. To check this we computed the work function of the planar film and Ru nanorods using the measured I-V curves. For this test, we used a bandpass filter to pass monochromatic light (220 nm wavelength) onto the flat Ru film and Ru nanorods samples. The stopping voltage was computed by drawing a straight line through the points around zero bias and dropping the thermal tail in the I-V curves. The thermal tail in the I-V curves is an artifact of the fact that the tests were performed at room temperature—this causes the Fermi-Dirac energy distribution function to approach the energy axis asymptotically. Having determined the stopping potential (V₀), the work function (Φ) was then calculated using the relation Φ = hν−eV₀. The measured work function for the planar Ru film was ~4.67 eV, which is quite close to the reported value of 4.71 eV for bulk Ru. For the nanorods the work function did not show any significant dependence on the rod length (in the 120–480 nm range) and the measured work functions (4.63–4.81 eV) were quite close to that of the flat Ru film. These small differences cannot account for the nearly 3.3 times increase [Fig. 1(c)] in the photocurrents observed in our experiments. We also performed tests (not shown here) to investigate changes in the reflectivity of the nanorod and flat film samples by testing them at various inclination angles with respect to the incident light. The results indicated that reflectivity changes are not significant for our system.

———

aAuthor to whom correspondence should be addressed; electronic mail: koratn@rpi.edu

Downloaded 13 Jun 2007 to 131.155.113.25. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp
Next we considered the surface area effect; the surface area of the nanostructured Ru surface is significantly greater than that of a planar Ru film. This means that even though the number of photons that are incident on the surface, which depends only on the light intensity, is the same in both cases, the number of surface atoms encountered by the incoming photons will be significantly greater for the nanostructured surface. This suggests that the probability of photon collection should be higher for the nanostructured surface compared to the planar film. We measured the surface area increase using atomic force microscopy of the Ru nanorod apex caps compared to a flat Ru film. Only the apex cap area of the nanorods was considered in the calculation since the pyramidal tapering geometry of the nanorods shields the sidewalls and only the apex caps of the nanorods are exposed to the incoming photons. Our measurements indicate that the surface area increase associated with the top exposed pyramidal caps is about the same for different rod lengths. Therefore we expect that at best a twofold increase in the photocurrents can be attributed to surface area effects. In addition to the area effect, another contributing factor to enhanced photoemission from the Ru nanocolumns could be their single crystal nature. For metals such as Ru, oxygen is shown to seep into the subsurface through the grain boundaries. This subsurface oxygen can also trap and scatter the excited photoelectrons. The Ru flat film is polycrystalline in nature and consequently the presence of grain boundaries can be expected to lower its electron escape probability compared to the Ru nanorods which are single crystals. Therefore it would appear that the single crystal nature of the nanorods together with the approximately twofold area increase associated with the nanorod apex caps is responsible for the enhancement in performance observed in our experiments.

Ru nanorod apex caps compared to a flat Ru film. Only the apex cap area of the nanorods was considered in the calculation since the pyramidal (tapering) geometry of the nanorods shields the sidewalls and only the apex caps of the nanorods are exposed to the incoming photons. Our measurements indicate that the surface area increase associated with the top (exposed) pyramidal caps is about the same (approximately two times) for different rod lengths. Therefore we expect that at best a twofold increase in the photocurrents can be attributed to surface area effects. In addition to the area effect, another contributing factor to enhanced photoemission from the Ru nanocolumns could be their single crystal nature. For metals such as Ru, oxygen is shown to seep into the subsurface through the grain boundaries. This subsurface oxygen can also trap and scatter the excited photoelectrons. The Ru flat film is polycrystalline in nature and consequently the presence of grain boundaries can be expected to lower its electron escape probability compared to the Ru nanorods which are single crystals. Therefore it would appear that the single crystal nature of the nanorods together with the approximately twofold area increase associated with the nanorod apex caps is responsible for the enhancement in performance observed in our experiments.

![FIG. 1.](image1.png)

**FIG. 1.** (Color online) (a) Left: Schematic shows the oblique angle deposition (OAD) technique with substrate rotation. Right: Scanning electron microscope (SEM) image shows the side view of Ru nanorods fabricated using OAD; pyramidal apex tip of the nanorods is apparent in the image. (b) Schematic of the test setup for characterization of photoemission response. (c) Photoemission current response of Ru nanorod samples of different lengths and planar Ru film over a range of collector voltages. The saturation photocurrent from the nanostructured samples is about 3.3 times greater than the planar film. Under negative bias, the photocurrents for all the samples asymptotically approach zero, displaying a significant thermal tail.

![FIG. 2.](image2.png)

**FIG. 2.** (Color online) SEM images of the top view and the side cross-sectional view of slanted nanorods for four different deposition angles ranging from $\theta = 45^\circ$ to $85^\circ$. The actual tilt angle ($\alpha$) of the rods with respect to the substrate normal is also marked out. As the deposition angle increases the shadowing effect comes into play and the columns start becoming isolated and more single crystalline in nature.
The vertically oriented nanorod arrays shown in Fig. 1(a) are clearly not optimized from the point of view of photoemission. This is because only the top caps of the nanorods are photoactive while the sidewalls do not contribute to the photocurrent. To further enhance the photoemissivity we investigated the response of inclined or slanted arrays. For inclined arrays in addition to the caps a portion of the sidewalls (adjoining the caps) is also exposed to the incoming photon flux. To grow the nanostructures vertically using oblique angle deposition, the substrate is continuously rotated at a constant angular velocity (0.5 Hz). Without substrate rotation, the nanorods grow tilted towards the incident flux as shown in Fig. 2; the inclination angle ($\alpha$) is generally smaller than the flux deposition angle ($\theta$). We chose five different slanted Ru nanorod samples with different deposition angles ($\theta = 30^\circ$, $45^\circ$, $60^\circ$, $75^\circ$, and $85^\circ$). Scanning electron microscope (SEM) characterization of the nanorods (Fig. 2) shows that for small deposition angles the rods are lumped together and resemble a polycrystalline film (e.g., for $\theta = 30^\circ$ and $45^\circ$, the columns are fused and there is no separation of the structures, hence they have a more or less flat and continuous surface). Therefore for small deposition angles we do not expect any significant difference between the response of the Ru nanorod samples and the Ru flat film. This is demonstrated in Fig. 3; the saturation photocurrent of the $30^\circ$ Ru nanorod sample is nearly identical to the flat film results shown in Fig. 1(c). As the deposition angle is increased ($\theta > 60^\circ$) the shadowing effect becomes more prominent and discrete (isolated) nanostructures are created. The photoactive area of these inclined rods is expected to be superior to vertically grown rods since in addition to the apex caps a portion of the sidewalls (adjoining the caps) is also photoactive. The test results indicate that for $60^\circ$ slanted deposition the photoemissive response of the nanorods is superior to the vertical rods. The saturation photocurrent for the $\theta = 75^\circ$ slanted nanorods is about 15-fold greater than a flat film, which is almost a five-fold improvement over the vertical rods. The fact that the photocurrent for $\theta = 75^\circ$ is more than that for $\theta = 85^\circ$ is corroborated by a recent theoretical study which showed that the enhancement in the nanorod surface area (caps and sidewalls adjoining the caps) by oblique angle deposition shows a maximum at a deposition angle of $\sim 75^\circ$. We also compared two Ru nanorod samples with the same deposition angle ($\theta = 75^\circ$) but with different heights (330 and 470 nm). The results (Fig. 3) indicated that the height of the slanted nanorods has no significant influence on photoemission; this is expected since the area of the sidewalls that are exposed to the photon flux depends only on the nanorod inclination angle and the nanorod-to-nanorod separation and is not affected by the nanorod length. We also compared the performance of a vertical Pt nanorod array with a slanted Pt array with $\theta = 85^\circ$. For both Ru and Pt, the ratio of the saturation currents of slanted rods (with $\theta = 85^\circ$) to vertical rods was about the same ($\sim 1.9$). This confirms that the enhancement in photocurrent for a slanted nanorod array compared to a vertical array is primarily an area effect and is material independent.

The results shown in this work indicate that nanostructured surfaces patterned by oblique angle deposition can exhibit better than an order of magnitude increase in photoemission compared with planar surfaces. This enhanced photoemissivity of nanostructured surfaces could result in the development of new photomultiplier systems with improved performance, thereby benefiting a variety of disciplines such as fluorescence spectroscopy to detect enzymes and biological and chemical tracers, chemiluminescence and bioluminescence detection, particle and high energy physics, radiation physics, forensics, robotics, high speed photography, gene chip scanners, and related medical diagnostic applications.

This work is supported by NSF NIRT Award Nos. 0403789 and 0506738 to two of the authors (N.K. and T.M.L.). The authors thank D.-X. Ye, T. Parker, and P.-I. Wang for taking the SEM pictures.

FIG. 3. (Color online) I-V curves for different slanted nanorod samples and the vertical rods. The slanted rods with $\theta = 85^\circ$ and $75^\circ$ show much larger photocurrents that the vertical rods, due to greater exposed surface area. For $\theta = 75^\circ$ the saturation photocurrent is over an order of magnitude ($\sim 15$-fold) larger than for a planar flat film. Similar to the vertical nanorods, the photoemission response of the slanted nanorods (with $\theta = 75^\circ$) is not significantly affected by the length (or height) of the rods.