Field ionization process is a subject of intense research because of its technological applications in ionization sensors and field ion microscope (FIM).\textsuperscript{1,2} The field required in ionization of gases is very high and can be of the order of few V/Å. Therefore, several kilovolts are applied to a sharp tip in order to draw any useful ionization currents. The enhancement in the electric field at the sharp tip apex due to its geometry has been realized by many researchers.\textsuperscript{3–5} Riley \textit{et al.}\textsuperscript{3} have demonstrated the detection of helium atoms via field ionization from protruding carbon nanotubes (CNT). In a recent study, Modi \textit{et al.}\textsuperscript{4} reported fabrication of a miniaturized gas ionization sensor using vertically aligned multilayered CNT. They showed smaller breakdown voltages (few hundred volts) for various gases including inert gases such as argon. Besides using CNT to produce high electric fields, report\textsuperscript{5} exist of using sharp metallic needle-type structures for gas ionization (in these studies few kV anode voltage was applied to W tips and \(~10\) nA ion current was obtained). In this letter, we show the efficient ionization properties of \(\beta\)-phase W nanorods for Ar gas. The sharp pyramidal apexes (or tips) of the W nanorods provide a large number of individual ionization sites that amplify the electric field by several orders of magnitude and enable field ionization at extremely low operating voltages. The W nanorods were grown by a glancing angle sputter deposition (GLAD) technique, which allows for single step fabrication of nanorods with desired geometry.\textsuperscript{6,7} GLAD is a physical vapor deposition in which flux arrives at a large oblique incidence angle (\(>80^\circ\)) from the substrate normal (while the substrate is rotating). This results in the formation of isolated nanorods by the self-shadowing mechanisms without lithography and multi-step processes. The onset voltage for argon ionization by W nanorods was observed to be only a few volts with the maximum ion currents ranging from about \(10^{-7}\) to \(10^{-4}\) A for Ar pressures ranging from \(10^{-5}\) to \(10^{-2}\) Torr. We have also shown that the Ag film cathode surface gets modified due to Ar ion bombardment during the field ionization measurements and we observed the formation of nanosize bubbles on the granular structure of Ag film surface.

Tungsten nanorods were grown on a native oxide covered polished \(p\)-Si(100) (resistivity \(12–25\) \(\Omega\) cm) substrate using a \(99.95\%\) pure W cathode in a dc planar magnetron sputtering chamber with a base pressure of \(1.4 \times 10^{-6}\) Torr. The sputtering power used was \(200\) W at an argon pressure of \(1.5\) mTorr. The vapor flux arrived at an oblique incidence angle \(\theta\) from the substrate normal. The angle \(\theta\) has been repetitively changed from large to smaller angles to obtain a layered structure in the vertical direction: \(85^\circ\) (40 min), \(75^\circ\) (10 min), and \(60^\circ\) (5 min) for the first layer and then three layers of \(88^\circ\) (10 min), \(85^\circ\) (10 min), \(80^\circ\) (5 min), \(75^\circ\) (10 min), and \(60^\circ\) (3 min). The deposition rate in all the experiments lies within \(7\) to \(10\) nm/min. The maximum temperature of the substrate during the deposition was \(80\) \(^\circ\)C. The limited adatom mobility combined with the shadowing effects due to the extremely oblique incidence with substrate rotating at \(0.5\) Hz resulted in the formation of isolated W nanorods having a pyramidal apex on each nanorod. The cross sectional and top views of scanning electron microscopy (SEM) images are shown in Figs. 1(a) and 1(b), respectively. The pyramidal shape tip apex with square base

![FIG. 1. (a) SEM top view of β phase W nanorods; (b) a schematic of the setup for Ar gas field ionization measurements. The cathode is a Ag film grown on a Si substrate that is a distance \(d=1162\) nm away from the anode made of β-phase W nanorods (shown as the SEM side view). The scale bars in both images are 100 nm. The voltage \(V\) is applied on the anode and the ion current \(I\) is measured.](image-url)
is clearly visible in Fig. 1(a) and the nanorods have an average length \((L)\) of 762±5 nm. In a separate x-ray diffraction measurement (not shown here) these nanorods were confirmed to be \(\beta\) phase.\(^6\)\(^,\)\(^7\) The formation of \(\beta\) phase in these W nanorods during GLAD growth results in the development of sharp square based pyramidal apexes.\(^7\)

The field ionization experiments were conducted in a separate ultrahigh vacuum (UHV) chamber with a base pressure better than \(5 \times 10^{-9}\) Torr. The schematic of the setup for the measurement of argon gas field ionization is shown in Fig. 1(b). The anode is the W nanorods sample and the cathode is a 1 \(\mu\)m thick continuous Ag film deposited over \(p\)-Si(100) surface. A piezo driven Inchworm\(^\text{®}\) motor was used to control the distance between W nanorods anode and Ag film cathode. A high purity (99.9999\%) research grade argon gas was admitted to the UHV chamber through a leak valve to various pressures ranging from \(10^{-5}\) to \(10^{-2}\) Torr. A positive voltage ranging between 0 and 400 V was applied to the W nanorods sample and the ionization current was collected at the Ag film cathode about 0.4 \(\mu\)m away from the W nanorods apex.

Figure 2 shows experimentally measured ionization current versus anode voltage for different Ar gas pressures ranging from \(10^{-5}\) to \(10^{-2}\) Torr and at zero Ar pressure or background vacuum. The ion current fluctuations were observed to be ±10\% for currents smaller than 100 nA and ±50\% for higher current values. The ion current was found to increase rapidly with increasing positive voltage applied to the nanorods sample, which is visible from the logarithmic scale in Fig. 2. A current–voltage curve for the background current, i.e., in the absence of Ar gas is also shown for comparison. Two findings from Fig. 2 are (i) the onset voltage for ionization of argon is only few (3–4 V) for all the argon gas pressures studied, whereas in the absence of argon (i.e., for a background vacuum of \(5 \times 10^{-9}\) Torr) it is about 220 V and (ii) the ion current collected with Ar gas (\(10^{-2}\) Torr) present is two orders of magnitude more than the background. This demonstrates outstanding and unambiguous gas detection with a favorable signal-to-noise ratio for these pyramidal W nanorods ionizers.

The strong voltage dependence of ion current in Fig. 2 can be attributed\(^8\) to a rapid increase in tunneling probability for electrons from impinging Ar atoms to the metal tip. Another important observation is that the increase in the ionization current is much more rapid for \(10^{-2}\) Torr Ar pressure compared with other lower gas pressures. This is because at higher gas pressure, secondary ionizations of Ar atoms between the nanorods anode and Ag film cathode may be possible (by the secondary electrons ejected from the Ag film cathode due to Ar ion impacts).

The local field within 1–2 nm close to the tip apex determines the barrier height and thickness through which electrons must tunnel from the Ar atoms to the anode. For sharp tip structures, the local field is enhanced by a field-enhancement factor \(\gamma\), with respect to the field strength \((V/d)\) for a simple parallel plate capacitor, where \(V\) is the voltage applied across the electrodes and \(d\) is the spacing between the parallel plates. The literature reports onset field strength for Ar ionization in the range of 0.5–1.0 V/Å.\(^9\) Using this onset field value we calculated the enhancement factor \(\gamma\) to be in the range of 1300–2600 for net anode–cathode spacing \(d\) of about 1162 nm [=length of nanorod (762 nm) +gap (400 nm)], see Fig. 1(b), and our observed ionization onset voltage of 3–4 V. Once we know \(\gamma\), we can estimate the nanorod tip apex radius \(\rho\) using a “hemisphere on a post” model \([\gamma=(2+L/\rho)(1-L/d)].\(^10\) This model relates the field enhancement factor \(\gamma\) to the nanorod tip radius \(\rho\), nanorod length \(L\), and net anode–cathode spacing \(d\). After putting all the known geometrical parameters \(L=762\) nm, \(d=1162\) nm, and \(\gamma\) (from 1300 to 2600) for nanorods in this model, we obtain the nanorod tip radius in the range of 0.1–0.2 nm. This is consistent with the presence of atomically sharp tip apex on \(\beta\)-phase W nanorods, which results in an extremely high field enhancement factor.

To investigate any possible damage to W nanorods anode and Ag film cathode structures after the field ionization experiment, we did surface topography measurements using atomic force microscopy (AFM). No noticeable change on the W tip surface was observed. In contrast, the Ag film cathode surface was significantly modified. Figure 3 shows 1 \(\mu\)m×1 \(\mu\)m AFM images of the Ag film before and after argon ionization experiments. The original Ag film [Fig. 3(a)] shows grain structure with an average grain size of about 105±18 nm on the surface. These grain surfaces were modified [Fig. 3(b)] by the argon ion impacts and nanosize (∼105 nm) bubble structures were formed. The bubble density was estimated to be about 10\(^{14}\) bubbles/m\(^2\), which is
higher than the nanorod density of $10^{13}$ nanorods/m$^2$. The depth range for Ar atoms was calculated from SRIM03 software\textsuperscript{11} to be 0.5 nm, indicating that argon ions get implanted as neutral atoms close to the cathode surface. Based on the measured ion current we estimated the fluence value to be $10^{20}$ ions/m$^2$. This high fluence value indicates that the formation of bubbles is not due to a single argon ion impact but is due to the clustering of argon atoms on the Ag film surface. Such types of bubbles form due to low solubility of inert gas atoms in solids.\textsuperscript{12}

In summary, we have shown that pyramidal $\beta$-phase W nanorods can ionize Ar gas at only few volts and provide ion currents of tens of microamperes depending on the gas pressure. One can use these $\beta$-phase W nanorods as a compact field ionizer safely operated by battery.

This work was supported by NSF DMR and NIRT Awards. The authors thank D.-X. Ye for taking SEM images.