Fabrication and Characterization of NiO based Metal−Insulator−Metal Diode using Langmuir-Blodgett Method for High Frequency Rectification

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Fabrication and characterization of NiO based metal–insulator–metal diode using Langmuir-Blodgett method for high frequency rectification

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(Received 26 April 2017; accepted 13 April 2018; published online 20 April 2018)

Thin film metal–insulator–metal (MIM) diodes have attracted significant attention for use in infrared energy harvesting and detection applications. As demonstrated over the past decades, MIM or metal-insulator-insulator-metal (MIIM) diodes can operate at the THz frequencies range by quantum tunneling of electrons. The aim of this work is to synthesize required ultra-thin insulating layers and fabricate MIM diodes using the Langmuir-Blodgett (LB) technique. The nickel stearate (NiSt) LB precursor film was deposited on glass, silicon (Si), ITO glass and gold coated silicon substrates. The photodesorption (UV exposure) and the thermodesorption (annealing at 100 °C and 350 °C) methods were used to remove organic components from the NiSt LB film and to achieve a uniform homogenous nickel oxide (NiO) film. These ultrathin NiO films were characterized by EDS, AFM, FTIR and cyclic voltammetry methods, respectively. The MIM diode was fabricated by depositing nickel (Ni) on the NiO film, all on a gold (Au) plated silicon (Si) substrate. The current (I)-voltage (V) characteristics of the fabricated diode were studied to understand the conduction mechanism assumed to be tunneling of electron through the ultra-thin insulating layer. The sensitivity of the diode was measured to be as high as 35 V⁻¹. The diode resistance was ∼100 ohms (at a bias voltage of 0.60 V), and the rectification ratio was about 22 (for a signal voltage of ±200 mV). At the bias point, the diode response demonstrated significant non-linearity and high asymmetry, which are very desirable characteristics for applications in infrared detection and harvesting. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5034455

I. INTRODUCTION

High-frequency diode rectifiers are very important for applications such as IR sensing,6–11 solar energy harvesting,12–14 THz electronics,12 THz mixing13 and display technologies.14 MIM/MIIM diodes are vigorously studied as high-frequency rectifiers1,3,15–21 for various applications. There are other types of diodes, such as geometric diodes,22,23 molecular diodes24,25 and carbon nanotube diodes,26 that are presently being investigated for high frequency rectification. Because of its high frequency response, the Schottky diode is widely used as a rectifier, however, Schottky diodes cannot operate efficiently at THz frequencies. A MIM diode, which is an ultra-thin insulator layer sandwiched between two metal electrodes, is a better rectifier compared to a Schottky diode beyond ∼12 THz.27,28 A potential barrier is formed between the Fermi level of the metal electrode and the conduction band of the insulator. The electrons tunnel through the potential barrier by applying a potential across the electrodes.29 Time constants in the femto-second (10⁻¹⁵ s)30 range make the quantum-based

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electron tunneling process a desired rectification technique in MIM structures. Therefore, well-designed MIM diodes could possibly be used as rectifiers at frequencies as high as $10^{15}$ Hz. However, effectively controlling the quantum mechanical electron tunneling through an ultrathin insulator is a major challenge in the development of high-performance MIM diodes.

Since the probability of quantum mechanical tunneling of electrons depends exponentially on the thickness of the insulator between the two metal electrodes, an insulating layer of a few nanometers is necessary for optimal behavior. Moreover, the insulating layer should be pinhole free, to avoid shorting of the two electrodes, and should be uniform and have a very low surface roughness to produce a uniform electric field across the entire device. These issues could be minimized by the careful fabrication of the insulating layer and the design of the active diode.

The insulator layer of the MIM diode can be grown by different deposition methods, such as e-beam, sputtering, vapor, thermal oxidation, anodic oxidation and atomic layer deposition (ALD). However, most of these techniques require complex systems and are expensive. Moreover, the deposition of an ultra-thin (a few nanometers thick) layer may contain pinholes and have a rough surface. The LB deposition is a low-cost technique that can produce a uniform, pinhole free and ultra-thin insulating layer with a high degree of structural order through a layer-by-layer deposition. The thickness of the film could be controlled by the number of LB monolayers deposited on the substrate. Most of the reports on the LB deposition technique reference organic film deposition. However, thin organic LB films could be easily damaged during the top metal deposition, solution processing or aging.

In this work, the synthesis of thin films of inorganic NiO from an organic precursor, nickel acetate, using the LB method, and its use as an insulating layer of a MIM tunnel diode is explored. In previously reported studies, NiO demonstrated a good high frequency response and sensitivity.

Nickel acetate was used as the subphase during the experiment and the spreading liquid was a solution of stearic acid and chloroform. The surface tension-area isotherms of the NiSt monolayer on the air-water interface were examined to find the target surface tension for the LB monolayer deposition. The monolayer formation parameters such as concentration of subphase, spreading volume and the deposition parameters such as barrier speed, lifting speed, and wait time were optimized to obtain a thin compact pinhole free monolayer. The NiSt monolayers were then deposited on different substrates, such as glass, Si, indium tin oxide (ITO) coated glass and Au coated substrates. The transfer ratio (ratio of the decreased area of the surface of the trough to the area of the dipped substrate) of the deposition process was monitored to observe the quality of the deposited multilayers. Then the organic component of these nickel acetate LB films was removed through photodesorption (UV exposure) and thermodesorption (annealing at 100 °C and 350 °C) in ambient air, leaving just the metal oxide layer on the substrate. Figure 1 shows a schematic of the NiO deposition process.
Furthermore, the composition, surface, electrochemical and optical properties of the thin NiO LB films were analyzed using energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), cyclic voltammetry and FTIR Spectroscopy, respectively. Finally, the quantum tunneling mechanism of electrons in the fabricated Ni-NiO-Au MIM diode was determined from the DC electrical measurements. Specifically, the rectification performance characterizing parameters such as sensitivity and turn-on voltage, were obtained from the DC I–V curves. Figure 2 shows a schematic of the Ni-NiO-Au/Cr MIM tunnel diode structure.

II. EXPERIMENTAL DETAILS

A. Materials

The nickel acetate tetrahydrate (Ni(CH₃COO)₂, ACS, 99.998% trace metals basis), stearic Acid (C₁₈H₃₆O₂, analytical standard, ≥ 98.5%), chloroform (CHCl₃, ACS reagent, ≥ 99.8%), acetone (CH₃COCH₃, ≥ 99.5% A.R.), methanol (CH₃OH, ≥ 99.8% A.R) and 2-propanol ((CH₃)₂CHOH, ≥ 99.5%, A.R., ethanol (C₂H₅OH, ≥ 99.5%, A.R.) were procured from Sigma-Aldrich. Ultra-pure water (18.2 MΩ cm) was used as sub-phase.

B. Synthesis of NiO multi layers

The NiO multilayers on different substrates were fabricated by using a method similar to that described by Schurr et al. The substrates were cleaned thoroughly using acetone, methanol and 2-propanol, sequentially. The substrates were rinsed thoroughly with ultra-pure water and dried at room temperature. The NiSt monolayers and multilayers were deposited on different substrates using a process similar to that reported earlier. A KSV NIMA Langmuir-Blodgett trough system equipped with a paper Wilhelmy plate was used to deposit multilayers on the substrates. The Wilhelmy plate was used to measure the surface tension of sub-phase at different concentrations by suspending in the subphase at trough. Nickel acetate and ultra-pure water were mixed to form the sub-phase at different concentrations. Varying volumes of 1 mg/ml stearic acid/chloroform solution were spread carefully using a micro-liter syringe to form a monolayer on the sub-phase. The monolayer deposition parameters can be obtained from surface tension-surface area (Π–A) isotherms. The deposition parameter was determined from the transfer ratio, which is the ratio of the decreased area at the sub-phase surface during deposition to the total substrate area. The feedback control system of the barrier compression of the trough promises a closely packed monolayer at the air-sub-phase surface. Subsequently, the substrate was dipped into the sub-phase, maintaining all deposition parameters, to transfer the monolayer from the air-subphase interface to the surface of the substrate. After deposition on the substrate, the organic components (hydro-carbon chain) are removed from the deposited
organic precursor film to obtain a NiO film. There are two ways to realize this: (i) heat up the film up to 350 °C under ambient conditions, (ii) irradiate the films with UV light at ambient conditions and afterwards heat the films at 350 °C in air. Even though both of these techniques can be used to remove the organic components from the deposited organic precursor film, the latter technique was used because it produces a smooth surface over the deposited area. The fabricated LB monolayers were treated under UV. The exposure time depends on the number of deposited LB layers. For the fabricated devices of 20 LB layers the exposure time was around 12 hours, whereas for 10 layer devices the exposure time was around 6 hours. Then the UV treated films were annealed at 100 °C for 15 mins as well as 350 °C for 120 mins to form the NiO multilayer.

From the surface tension-surface area (Π-A) isotherms different substrates, monolayer formation parameters, such as sub-phase concentration, spreading liquid volume, barrier speed and evaporation time were optimized before deposition of the precursor film of NiSt. The target pressure, wait time and dipping/lifting speed were optimized for the transfer ratio to be maintained close to one during deposition.

Energy Dispersive X-ray Spectroscopy (EDS) was used to investigate the components in the films before and after the treatment. A Hitachi S-800 field emission scanning electron microscope (FE-SEM) was used for this experiment with a scan range of 0 – 9 keV.

An AFM (Digital Instrument Co., USA) with a Bruker AFM probe tip (0.01-0.025 Ohm-cm Antimony (n) doped Si) in the tapping mode was used to observe the film surface morphology.

A Voltalab PGZ301 system was used for the electrochemical analysis of NiO films over conducting indium tin oxide coated (ITO) glass plate. The measurements were performed in a cell containing three electrodes. The NiO processed from NiSt LB films on ITO coated glass plate operated as working electrode, a platinum wire used as the counter electrode, and Ag/AgCl as reference electrode in a 0.1 M HCl based electrolytic solution.

Infrared (IR) spectroscopy was performed using a Perkin Elmer Spectrum ONE FTIR Spectrometer on the NiO film in transmission mode. For measurement purposes, IR transparent Si was used as a substrate.

DC I-V measurements were carried out to characterize the diode performance. The diode consisted of a 100 nm Au/Cr layer (bottom electrode) deposited on a Si/SiO₂ substrate (Cr being used as an adhesion layer). In separate runs, 10 and 20 layers of nickel acetate monolayers were deposited on the Au/Cr layer using the LB technique. The multilayers were then exposed to UV and annealed at different temperatures to produce the NiO insulating thin film. Finally, the top 50 nm thick Ni electrode was deposited by sputtering, at a pressure of 2-3 mtorr and 80 watts of power, using a shadow mask to control the shape and size of the top contact. To measure the current-voltage characteristics of the Ni-NiO-Au/Cr MIM diodes, a micro-manipulator setup with Dumet (Cu-Fe) probe tips was used. A 4145B Semiconductor Parameter Analyzer was used to analyze the measurements.

III. RESULTS AND DISCUSSION

A. LB film

Figure 3 shows the surface tension-surface area (Π-A) isotherms of the monolayer at different sub-phase (nickel acetate) concentrations formed at the air-water interface. During the experiments, the sub-phase concentrations were 1.0, 0.1, 0.05 and 0.01 mmol/l while the spreading volume of stearic acid, sub phase volume, wait time and barrier speed were maintained at 14 µl, 65 ml 20 min and the 5 mm/min respectively. As shown in figure 3, the isotherms of nickel acetate have different collapse points for different concentrations of the sub-phase. The molecules at the surface have different intermolecular distances at different concentrations of the sub-phase. The inter-molecular distance for lower concentrations is high and for higher concentrations is low. When the surface tension increases, when the barrier starts compressing, and reaches a certain point where the inter-molecular force is very high and the inter-molecular distance is very small, the highest point suggests the collapse point. At that instant, a compact monolayer has been formed at the air-sub-phase interface. Further increase in the surface tension (compression of the barrier) results in the collapse and overlapping of monolayers, and the intermolecular force has been found to drop significantly. At higher concentrations of nickel
acetate (1.0 mmol/l), more Ni ions react with stearic acid to form a somewhat overlapped monolayer which has not shown any prominent collapse/drop in the surface tension (green line). The surface tension keeps increasing even after the collapse point. Moreover, the collapse points are prominent at lower concentrations (0.1, red line, 0.05, yellow line and 0.01, blue line mmol/l) suggesting that no overlapping monolayers would exist at those concentrations of nickel acetate. The collapse point for 0.1 mmol/l (red line) is higher than that of 0.05 (yellow line) and 0.01 mmol/l (blue line) indicating a more compact monolayer at that point. Thus, at a phase concentration of 0.1 mmol/l a compact NiSt monolayer could be formed.

Figure 4 depicts the surface tension-surface area (Π-A) isotherms of NiSt monolayer at different spreading volumes (12, 14 and 16 µl) of Stearic acid. The sub-phase concentration of 0.1 mmol/l was maintained during carrying out the experiments. From the figure, the shape and the trend of the graphs have no differences but the collapse point shifts towards right with higher spreading volume.
With higher spreading volume, the number of molecules at air-water interface increases and which raises the inter-molecular force and decreases the inter-molecular distances. As the inter-molecular distance decreases, the collapse pressure point could appear early for higher spreading volume. It provides enough space to the barrier of the trough to maintain target pressure. On the other hand, a lower number of molecules on air-water interface (lower spreading value) gives enough time for self-orientation to obtain well-ordered monolayer at the air-water interface. Considering all these, 14µl of spreading volume might be better to use to fabricate the Langmuir monolayer. The compactness of the monolayer deposited on a solid surface were found by supervising the transfer ratio which is computed during each deposition. Values between 0.8-1.0 are considered as good transfer ratio. Several experiments have been carried out to optimize the deposition parameters such as dipping speed (up 4 mm/min and down 2 mm/min), barrier speed (3 mm/min), wait time (500 s) and target pressure (20 mN/m) to get the best monolayer configuration. For all the experiments sub-phase volume was maintained at 65 ml.

B. AFM studies

Atomic force microscopy (AFM) was used to obtain and compare the surface morphology of the deposited films both before (Figure 5a; NiSt) and after the treatment (Figure 5a; NiO). Figure 5 shows the AFM image of a representative area of the deposited films on a Si substrate. The average roughness, \( R_a \), of the deposited film was measured to be 4.5 nm for 10 LB layers whereas the root-mean-square (rms) value was found to be 3.4 nm. After the treatment (UV exposure and then consecutive annealing), both of the measurement values dropped to 1.2 and 1.6 nm. All the measurements were performed over an area of 100 µm². The thicker and rougher layer as deposited showed in Figure 5(a) became smoother and thinner after treatment, as depicted in Figure 5(b). The reduced roughness endorses that after the UV exposure and high temperature treatment the resulting layer is a thin layer of NiO. From the section analyses it is also apparent that after UV exposure and subsequent annealing the deposited film surface becomes somewhat flat. The Bruker AFM tips (0.01-0.025 ohm-cm antimony (n) doped Si) were used for this purpose. These values of roughness have to be compared with the typical value of \( R_a = 0.5 \) nm for silicon wafers. This concept was further confirmed from the EDS and FTIR results.

Moreover, the roughness of the bottom electrode was around 1.104 nm which implies that the gold electrode layer is quite conformal to the bottom substrate. After treatment, the RMS roughness of the gold electrode was \( \sim 1.3 \) nm. The annealing process didn’t introduce any significant roughness.

C. EDS studies

The EDS method was employed to identify the existence of Ni and O in the synthesized layer and to understand the consequence of the post-deposition treatment. The measurement was carried
out on a NiO monolayer both before and after treatment. The results are depicted in Figure 6. As shown in Figure 6(a), the EDS pattern for the NiO monolayer before treatment shows peaks that correspond to Si, O, Ni, and C. Ni, C, and H comprises NiSt film on the substrate. The O peak is obtained from the native SiO$_2$. The H is not noticeable by EDS. On the other hand, the EDS pattern for the NiO monolayer after treatment only demonstrates peaks corresponding to Si, O and Ni, with no detectable peak for C. Hence, these results endorse the formation of NiO from Ni-St after UV exposure and subsequent annealing.53,54

D. FTIR studies

FTIR analysis was performed to obtain additional evidence of NiO formation from LB films of NiSt precursor. Figure 7 shows FTIR spectra of a 20 LB monolayer of NiSt (before treatment) on an IR transparent silicon substrate and the NiO layers fabricated (after treatment) of the SA LB precursor film. NiSt LB films (blue color) show peaks at 2848 and 2920 cm$^{-1}$ due to the symmetric

FIG. 6. EDS spectrum of (a) the as deposited Ni-St thin film and (b) treated NiO thin film.
and asymmetric methyl stretching bands. Also the peaks observed at 1538 and 1570 cm\(^{-1}\) are due to the carbohydrate group, indicative of the antisymmetric ν\(\text{COO}^-\) and also the ν\(\text{CH}_3\) bands.\(^{55}\) The broad peaks at 1650 cm\(^{-1}\) is due to water hydration.\(^{56,57}\) However, the treated NiO (orange color) does not show the characteristic peaks of 2848 and 2920 cm\(^{-1}\), of 1650 cm\(^{-1}\) and of 1538 and 1570 cm\(^{-1}\), suggesting the removal of organic components and the formation of a NiO film from the organic precursor LB films. Moreover, a metal oxide such as NiO generally contributes absorption bands below 800 cm\(^{-1}\) arising from inter-atomic vibrations. The peak at 460 cm\(^{-1}\) shows Ni–O stretching vibration which is a strong indication of the presence of the NiO film on the substrate.\(^{57-59}\)

E. Cyclic voltammetry

Figure 8 shows the cyclic voltammograms of a NiO thin film on ITO glass substrate in 0.1 M HCl at scan rates of 5, 10, 20, 50 and 100 mV/s. The oxidation peaks are observed at -0.45V, -0.38V, -0.38V, -0.37 V and -0.35 V for 5 mV/s, 10 mV/s, 20 mV/s, 50 mV/s and 100 mV/s whereas a reduction
peak is observed at -0.65 V regardless of scan rate. There is a sequential change of the oxidation peak potential from 5 mV/s to 100 mV/s for the NiO film on the ITO substrate. Buorgault et al. have shown the oxidation potential of NiO to be -0.49 V, which is close to our obtained oxidation potential between -0.45 to -0.35 V in 0.1 M HCl electrolytic solution at various scan rates. The change in the peak potential and the shape of the CVs indicate the quasi-reversible process. The CV results strongly suggest the formation of a NiO film after thermal annealing of nickel oxide LB films.

F. I-V characteristics

A HP 4145B semiconductor parameter analyzer along with a micro-manipulator setup was used to measure the current (I)-voltage (V) characteristics of the fabricated diode. Figure 9(a) (20 LB layers) and 10(a) (10 LB layers) show the typical I-V characteristics of the fabricated Ni-NiO-Au MIM diodes. The MIM diode was realized by sandwiching the insulating NiO LB layer between the Ni and Gold metal layers. The thickness of the gold layer was maintained at 100 nm considering its de-wetting nature. Below ~0.6 volts, the diodes show linear behavior making it inappropriate for
rectification. On the other hand, above 0.6 volts non-linear responses were exhibited by the diodes as a function of the barrier height and thickness of the insulating NiO layer. The thickness of the NiO was calculated to be $\sim 2.6 - 4.2$ nm for 10 monolayers of Ni-St.\textsuperscript{63,64} The 10 monolayer MIM diodes exhibit higher conductivity and lower turn on voltage than the 20 monolayer diode, supporting the assumption of the quantum tunneling conduction mechanism of the MIM diode.\textsuperscript{65}

The resulting I-V behavior of the fabricated diode was quantified by examining the current sensitivity and rectification ratio. These parameters were typically used to estimate the rectification capability traits of the MIM diodes.\textsuperscript{7} The conductivity is obtained from the 1\textsuperscript{st} derivative ($I'=dI/dV$) whereas the non-linearity is obtained from the 2\textsuperscript{nd} derivative ($I''=d^2I/dV^2$).

The sensitivity, a measure of a diode’s rectification capability, is defined as the ratio of the 2\textsuperscript{nd} derivative to the 1\textsuperscript{st} derivative.\textsuperscript{6,66} Based on the I-V characteristics of our specific MIM diode, to obtain maximum sensitivity the diode needs to be biased at 0.6 V. Fabrication of 20 monolayer and 10 monolayer diodes showed a maximum sensitivity of $\sim 28$ V\textsuperscript{-1} and 35 V\textsuperscript{-1}, respectively, which are high enough for effective rectification.\textsuperscript{17,40} A total of 20 devices were fabricated for each of the
10 and 20 layers with yields > 70%. For the 10 layer devices, the average value of sensitivity was \( \sim 32 \text{ V}^{-1} \) with a rectification ratio of \( \sim 21 \), for a \( \pm 200 \text{ mV} \) deviation from the 0.6 V bias point. For the 20 layer devices, the average value of sensitivity was \( \sim 27 \text{ V}^{-1} \) with a rectification ratio of \( \sim 19 \), for a \( \pm 200 \text{ mV} \) deviation from the 0.6 V bias point. It was observed that the roughness of the thicker films is higher than the thinner films, where thickness is in terms of number of monolayers. As the roughness increases, the electric filed varies throughout the device area. The asymmetry is calculated from the polynomial fit of the I-V curve of the devices. From I-V curve, we can see that the low voltage (<0.6V) currents in 20 cycle devices is higher than the 10 cycle devices. This might be because of the enhanced electric filed due to the higher roughness of the insulator layer. The enhanced electric field produces more current in the low voltage region in 20 cycle devices compared to 10 cycle devices. To get the higher asymmetry, tunneling current before the turn on point should be as low as possible. In 20 cycle devices higher current, compared to 10 cycle device, conducts through the insulator before the turn on point slightly reduces the asymmetry of the devices. The maximum and average values of the figures of merit were very close which implies good reproducibility and stability of the electrical measurements.

The rectification ratio, the other figure of merit, is defined as the ratio of the forward current to the reverse current, \( |I_f/I_r| \) for an equal swing of signal voltage (\( \Delta V \text{ volts} \)) centered at the bias point. In this experiment the rectification ratio for the highest sensitive device was calculated for different \( \Delta V \) centering at bias voltage of 0.6 volts. Figure 11 shows the rectification ratio of 10 layer device at different \( \Delta V \) centered at 0.6 volts. Inset shows the rectification ratio at low voltage. Since the difference between the forward (\( I_f \)) current and the reverse (\( I_r \)) current is small so the rectification ratio is very low (<4) for smaller swing of signal (10, 20, 30, 50, 100 mV). As the swing of the signal (\( \Delta V \)) increases, the forward current (\( I_f \)) increases due tunneling current for positive voltage as a result the rectification ratio becomes high for large swing of signal (\( \Delta V \)). The rectification ratio for 10 layer device was calculated to be \( \sim 22 \) for a \( \pm 200 \text{ mV} \) deviation from the 0.6 V bias point.

In order to interpret these results, it is necessary to consider the energy-band diagram of the device. Figure 12 shows the energy-band diagram of Ni-NiO-Au structured MIM diode at different bias conditions. Figure 12(a) shows the equilibrium band diagram of asymmetric MIM diode where \( \phi_{b1} \) and \( \phi_{b2} \) shows the barrier heights at Ni/NiO interface and NiO/Au interface respectively. In this research, Au and Ni were used as electrodes with work functions of 5.1 and 5.15 eV respectively. The difference in the work function is 50 meV which is rather small, however, a large work function difference is not required to achieve our objective. For our specific MIM diode a bias of 0.6 V is chosen to achieve maximum rectification.

Since the work function of Au is lower than Ni, the barrier height is slightly smaller on the Au electrode side as shown in Fig. 12(a). Figures 12(b) and (c) show the band diagram of the Ni-NiO-Au

![Rectification Ratio vs ΔV](image_url)
MIM diode under positive and negative bias conditions. To bias the device, a voltage was applied to Au electrode while keeping the Ni electrode at ground.

The electrical characterization of the fabricated devices were tested in the intermediate voltage (0 < V < \varphi / e) range. When a positive bias voltage is applied to gold (Au) electrode, the fermi energy (E_F) level of Au goes below the E_F of Nickel (Ni) electrode. As result, the electrons from Ni electrode can tunnel through the insulating layer to the Au electrode. As the thickness of the insulator in less than 10 nm, electrons can directly tunnel though the thin insulator film. As the voltage increases, the tunneling current increases according to Simmon's equation. The measurements were performed under isothermal condition (at room temperature), thermally-assisted tunneling can be neglected. For a negative bias voltage, the fermi energy (E_F) level of Au goes above the E_F of Nickel (Ni) electrode. As result, the electrons from Au electrode can tunnel through the insulating layer to the Ni electrode, which is in the reverse direction of previous condition. As the work function difference is very low between the Au and Ni electrodes, the I-V curve is rather symmetrical. From the I-V curves of the devices, figure 9(a) and 10(a), we can see that the tunneling current is higher in 10 monolayer devices is higher than the 20 monolayer devices. This because of the quantum tunneling mechanism is exponentially depend on the width of the potential barrier layer (thickness insulator layer). The current density curves (figure 9(e) and 10(e)) also show that the tunneling currents increase exponentially with increasing voltage. As the thickness of the insulator layer decreases, width potential of the potential barrier decreases, conduction of electrons through the insulator due to quantum tunneling mechanism increases.

The work function is an important parameter and affects the device performance, however it doesn’t uniquely control the FOMs of the MIM diode. Since the electrode and the insulator roughness could play a dominant role in the I-V characteristics, even overpowering the metal work function, the impact of these surface parameters of the interfaces also need to be considered.

As we have presented in this work, the surface roughness of the insulator and the underlying electrode after treatment is quite low and the layers are conformal to each other. As a result, a uniform electric field is maintained over the device area which leads to the low direct tunneling current before the non-linear part of the I-V curve. This increases the ratio of tunneling current before turn on to the tunneling current after turn on, resulting in high rectification and non-linearity at the bias point.
TABLE I. State-of-The-Art Diode Sensitivity.

<table>
<thead>
<tr>
<th>Work</th>
<th>Diode</th>
<th>Insulator Deposition Technique</th>
<th>Maximum Sensitivity (V$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hoofring et al.</td>
<td>Ni-NiO-Au (0.64 $\mu$m$^2$)</td>
<td>Oxidation</td>
<td>5.5</td>
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<td>Wilke, et al.</td>
<td>Ni-NiO-Ni (0.056 $\mu$m$^2$)</td>
<td>Sputtering</td>
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<tr>
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<td>Ni-NiO-Ni (0.075 $\mu$m$^2$)</td>
<td>Sputtering</td>
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<tr>
<td>Esfandiar et al.</td>
<td>Ni-NiO-Pt (0.0025 $\mu$m$^2$)</td>
<td>Oxidation</td>
<td>-13</td>
</tr>
<tr>
<td>S. Krishnan et al.</td>
<td>Ni-NiO-Cr (1.45 $\mu$m$^2$)</td>
<td>Oxidation + Sputtering</td>
<td>5</td>
</tr>
<tr>
<td>Choi et al.</td>
<td>Planar polysilicon CIC (60 nm$^2$) Boiling water Oxidation</td>
<td>-31</td>
<td></td>
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<tr>
<td>Dagenais et al.</td>
<td>Polysilicon-SiO$_2$-Ti/Au (0.35 $\mu$m$^2$) Boiling water Oxidation</td>
<td>-14.5</td>
<td></td>
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<tr>
<td>Bean et al.</td>
<td>Al$_2$O$_3$-Pt (0.005625 $\mu$m$^2$) Oxidation</td>
<td>-2.3</td>
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<tr>
<td>Zhang et al.</td>
<td>Ni-NiO-Cu (0.008 $\mu$m$^2$)</td>
<td>Thermal Oxidation</td>
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<tr>
<td>Gadalla et al.</td>
<td>Cu-CuO-Au (0.0045 $\mu$m$^2$)</td>
<td>ALD</td>
<td>6</td>
</tr>
<tr>
<td>Singh et al.</td>
<td>NiNiOx-ZnO-Cr/Au(400 $\mu$m$^2$)</td>
<td>Sputtering</td>
<td>16</td>
</tr>
<tr>
<td>Zhuang et al.</td>
<td>Ni-NiO-Ag (0.00031 $\mu$m$^2$)</td>
<td>Electrochemical</td>
<td>8.5</td>
</tr>
<tr>
<td>Azad et al.</td>
<td>Au-ZnO-Ni (0.44 mm$^2$)</td>
<td>Langmuir-Blodgett</td>
<td>32</td>
</tr>
<tr>
<td>This work</td>
<td>Au-NiO-Ni (0.44 mm$^2$)</td>
<td>Langmuir-Blodgett</td>
<td>35</td>
</tr>
</tbody>
</table>

The fabricated MIM diodes demonstrated a competitive sensitivity compared to previously reported results$^{70–75}$ as shown in Table I.

IV. CONCLUSIONS

A Rectenna, antenna coupled with a MIM diode, could be used as an IR detector or thermal energy harvester by a suitable choice of an antenna and a quantum tunneling MIM diode. Two figures-of-merit, that is, the turn-on voltage and the sensitivity, can determine whether a Rectenna could be used as an IR detector or energy harvester. The insulating layer of the MIM diode must be as uniform and thin as possible, as well as pinhole free for the optimal performance of the diode. In this work, the LB method was successfully employed to fabricate Ni-NiO-Au MIM diodes. A NiSt monolayer was formed at the air-water interface while using nickel acetate and stearic acid/chloroform solution as a sub-phase and spreading liquid, respectively. The NiSt monolayer was then deposited on SiO$_2$, Glass, ITO and gold plated SiO$_2$/Si substrates. The multilayers of NiSt were then treated with UV and subsequently annealed at 100 $^\circ$C for 15 min and 350 $^\circ$C for 120 mins to obtain a homogenous uniform NiO layer. Ten monolayers of NiSt produced an average NiO thin film roughness of 1.2 nm, indicating a highly uniform and flat surface. The MIM diode was made by depositing the NiO LB film on a gold-plated Si wafer and then sandwiched by a top Ni layer. The thickness of the bottom electrode (Au) of the MIM diode was maintained at 100nm to avoid de-wetting. The I-V characteristics of the fabricated diodes, of different insulator thickness, were successfully measured and used to understand the conductivity, nonlinearity and sensitivity of the diode. A rectification ratio of $\sim$22 was calculated at a bias voltage of 0.6 V for $\pm$200mV. A measured sensitivity value as high as 35 V$^{-1}$ reveals that the diodes have the potential to be used as rectifiers. The high diode I-V characteristics nonlinearity at a bias of 0.6 volts suggests that the studied diode is a great candidate for IR THz detection.

SUPPLEMENTARY MATERIAL

See supplementary material for the image of the KSV NIMA Langmuir Blodgett instrumental setup used for the fabrication process.

ACKNOWLEDGMENTS

The authors are thankful to National Science Foundation (NSF) for financial support under the NSF ECCS award number 1343228.


7 B. Berland, “Photovoltaic technologies beyond the horizon: Optical rectenna solar cell” (2003).


