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A novel surface area to volume ratio estimation technique for nanohemisphere contacted Schottky barrier structures

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Nanostructured metal-semiconductor interfaces, also known as Schottky barriers, exhibit remarkable electronic properties. The surface morphology of nanostructure contacted Schottky barriers has a significant effect on its current-voltage (I-V) characteristics, which is crucial for high-performance device applications. In this work, we present a surface area to volume ratio (SVR) estimation technique for nanohemisphere Schottky interfaces. By applying Gauss’s law, i.e. without deviating from first principle, we expand the formulation of thermionic emission theory to incorporate surface area and volume. The proposed technique has been assessed by comparison against AFM measured surface characteristics of fabricated Pt/ZnO nanohemisphere structures. Results show that the proposed technique has a high accuracy to within several percent from surface measurements. This technique provides access to SVR while eliminating the need for direct surface characterization, which can be an instrumental tool for the design and analysis of surface-sensitive devices, such as sensors. © 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/10.1063/1.5039722

INTRODUCTION

Schottky barriers formed between a transition metal and a semiconductor are widely used in high-performance electronic device applications.1,2 For a large subclass of these devices, such as solid-state gas sensors, the metal-semiconductor contact area and morphology often play a key role in device performance.3 Contact geometry is also strongly coupled with barrier I-V characteristics.4 Therefore, contact surface properties are of crucial importance.

Thermionic emission (TE) is arguably the most well-developed theory for describing carrier transport across a Schottky barrier.5–7 The Schottky-Mott relationship incorporates the contact area parameter, which links electrical characteristics to contact geometry.8,9 However, this theory assumes the contact area is reasonably flat, which is no longer applicable since the advent of devices with nanostructured contacts.5 In addition, small contact sized and nanostructured morphology lead to the formation of unique electronic band structures that alters carrier transport. Since nanostructured devices with large contact areas and unique contact morphologies give rise to localized charge distribution and electric field at the interface, carrier transport deviates from classical TE equations describing bulk materials and devices.10 Therefore, the classical TE model is no longer adequate in describing and predicting the characteristics of many modern devices.

The surface area to volume ratio (SVR) is a geometrical representation of the surface morphology, capturing the surface area as well as the volume occupied by the surface nanostructures. To obtain the SVR, various approaches have been reported in estimating the surface area of nanostructures. In terms of theoretical approaches, while a method was proposed to analyse the surface topography, it is limited to providing the surface roughness.11 While the Barrett-Joyner-Halenda (BJH) theoretical method are
applied to the desorption component of isotherm hysteresis, allowing the average mesopore diameter to be estimated, the technique can only be applied to nanoporous materials.\textsuperscript{12} In terms of experimental approaches, gas adsorption based methods,\textsuperscript{13} such as Langmuir\textsuperscript{14} and Brunauer-Emmett-Teller (N\textsubscript{2}-BET) isotherms,\textsuperscript{15} are perhaps the most widely adopted. However, these approaches involve introducing gases onto the material surface, which requires highly specialized equipment. In addition, obtaining accurate results require careful consideration of the type of gases employed, as well as the surface morphology and chemical composition of the sample.

In this work, we present a surface area to volume ratio estimation technique for metal-semiconductor (Schottky) barriers. By applying Gauss’s law, i.e. without deviating from first principle, we have expanded the formulation of thermonic emission theory to incorporate surface area and nanostucture volume. The accuracy of the proposed technique is then evaluated by comparing the estimation against AFM measured surface information from fabricated Pt/ZnO nanostructured thin-films. Results show that the proposed technique has a high accuracy of within several percent from actual measurements. The proposed technique provides an alternative to obtaining surface information based on \textit{I-V} curves, thus eliminating the need for material surface characterization.

### THEORY

The proposed SVR estimation technique is ultimately derived from first principles. The electron transport mechanism of high quality Schottky barriers based on metal-semiconductor interface can be modeled using TE theory,\textsuperscript{5} which in its existing formulation, does not include surface characteristics. However, we propose that, by using Gauss’s law, electric field can be expressed in terms of surface area and the volume occupied by surface features, thereby incorporating geometry characteristics into the TE formulation. Fig. 1 depicts the structure of a Schottky interface with a contact surface morphology modelled as an array of nanohemispheres. Fig. 2 depicts the energy bands of the Schottky interface. To reach equilibrium, changes in the electronic band structure occur. A depletion region is created in the oxide as a result of a realignment of space charges at the interface, establishing the so called ideal Schottky barrier height $\phi_i$. In a practical interface, the space charge density is influenced by defects, which leads to barrier height lowering $\Delta \phi$. The barrier height is described by the classical Schottky-Mott relationship as:\textsuperscript{5}

$$\phi_B = \phi_i - \Delta \phi$$

(1)

where,

$$\phi_i = \Phi_M - \chi_{SC}$$

(2)

where $\Phi_M$ is the metal work function, and $\chi_{SC}$ is the electron affinity of the semiconductor. Barrier height lowering ($\Delta \phi$) can be expressed in terms of the electric field $\xi$, as given by:

$$\Delta \phi = \sqrt{\frac{q\xi^4}{4\pi\varepsilon_s}}$$

(3)

where $\varepsilon_s$ is the permittivity of the semiconductor (typically $3.26\times10^{-11}$ F·m$^{-1}$ for ZnO).\textsuperscript{16}

![FIG. 1.](image) (a) Schematic of fabricated Schottky interface based on Pt contacted ZnO nanohemispheres. Back ohmic contact is also depicted. (b) Enlarged view of an individual Pt/ZnO nanohemisphere, with an electric field emitting from the surface due to the presence of space charges.
FIG. 2. Energy band diagram at the metal and n-type metal-oxide interface. An ideal Schottky barrier height $\phi_i$ is created as the interface is formed between the metal and metal-oxide. A nanostructured morphology allows greater space charges to accumulate at the interface, and thus the Schottky barrier height $\phi_B$ is further modulated by barrier height lowering $\Delta \phi$.

The $I$-$V$ relationship of a Schottky barrier is given by:

$$I = I_S \left[ \exp \left( \frac{q(V - IR_S)}{nkT} \right) - 1 \right]$$

where $q$ is the elementary charge, $V$ is the applied voltage across the interface, $R_S$ is the contact series resistance, and $\eta$ is the ideality factor. $I_S$ is the saturation current, which is a key parameter that is to be extracted experimentally (rather conveniently) via $I$-$V$ data. To continue the derivation of relating SVR in terms of $I_S$, we proceed to express $I_S$ analytically, given by:

$$I_S = A A^* T^2 e^{-\frac{\phi B}{kT}}$$

which can be rearranged for the barrier height, given by:

$$\phi_B = \frac{\eta kT}{q} \ln \left( \frac{A A^* T^2}{I_S} \right)$$

where $T$ is the temperature, $A$ is the Schottky contact area, and $A^*$ is the effective Richardson constant (e.g., for ZnO, 32 A cm$^{-2}$ K$^{-2}$). The parameter $\xi$, which can be expressed in terms of the space charge density $N_D$, is given by:

$$\xi = \sqrt{\frac{2qN_D}{\varepsilon_s} \left( \phi_B - \frac{kT}{q} \right)}$$

To express the barrier height lowering $\Delta \phi$ in terms of $N_D$, we substitute Eq. (6) into Eq. (3) to obtain

$$\Delta \phi = \left[ \frac{q^3 N_D}{8\pi \varepsilon_s} \left( \phi_B - \frac{kT}{q} \right) \right]^{1/4}$$

Then, we proceed to express $\xi$ in terms of the extracted $I_S$. Eq. (3) can be rearranged as

$$\xi = \frac{4\pi \varepsilon_s}{q} \Delta \phi^2$$

Substituting Eq. (5) into Eq. (8), therefore

$$\xi = \frac{4\pi \varepsilon_s T^2}{q} \left( \Phi_M - \chi_{SC} - \frac{nk}{q} \ln \left( \frac{A A^* T^2}{I_S} \right) \right)^2$$

Eq. (9) is an important result, as $\xi$ is expressed in terms of parameters that can be obtained from standard references, and that $I_S$ can be readily obtained from $I$-$V$ measurement.
In order to relate the electric field irradiated from the nanostructures $\xi$ to $\text{SVR}$, Gauss’s law is applied. Observing that integrating $\xi$ over the interface area is equivalent to integrating the charge density over the nanohemisphere volume (see Fig. 2(b)), Gauss’s law takes the following expression when applied to the Schottky interface as:

$$\int \xi dA = \frac{q}{\varepsilon_S} \int N_D dV$$

(10)

where, the surface potential of the nanostructured oxide is dependent on the surface area $A$ and nanostructured volume $V$.

Performing the integration, Eq. (10) becomes

$$\xi = \frac{q N_D}{\varepsilon_S} \left( \frac{V}{A} \right)$$

(11)

which is in terms of the nanohemisphere surface area and volume. Recognizing $\text{SVR} = V/A$, we can express $\xi$ in terms of $\text{SVR}$ as:

$$\xi = \frac{q N_D}{\varepsilon_S} \left( \frac{1}{\text{SVR}} \right)$$

(12)

or equivalently

$$\text{SVR} = \frac{q N_D}{\varepsilon_S} \left( \frac{1}{\xi} \right)$$

(13)

Substituting Eq. (9) into Eq. (13),

$$\text{SVR} = \frac{q^2 N_D}{4 \pi T^2 \varepsilon_S^2} \left( \Phi_M - \chi_{SC} - \frac{\eta k}{q} \ln \left( \frac{AA^* T^2}{I_S} \right) \right)^{-2}$$

(14)

where $\text{SVR}$ is expressed in terms of known physical parameters and the saturation current $I_S$, which can be obtained from references and measured $I$-$V$ data, respectively. It is worth noting that the proposed method is valid for all surfaces that are fully depleted, i.e. the space charge region completely fills the hemisphere. Interfaces with small hemisphere radii and are lightly to moderately doped generally satisfy this condition.

**EXPERIMENTAL**

To evaluate the proposed technique, $\text{SVR}$ is estimated by using Eq. (14), with numerical values extracted from $I$-$V$ measurement. For verification of the technique, the estimated $\text{SVR}$ is then compared to the measured $\text{SVR}$ obtained via AFM.

Twelve thin-films of ZnO nanohemisphere array were prepared by pulse laser deposition (PLD). Prior to deposition, the substrates were heated to 200 °C. A mixture of Ar:O$_2$ gas was injected into the chamber at a rate of 24:6 sccm until a working pressure of 0.133 mbar was reached. The deposition chamber was then pumped down to a base pressure of $5 \times 10^{-4}$ mbar. During deposition, a KrF (248 nm) excimer laser maintained an output power of 300 J, pulsed at 5 Hz. The laser beam was focused onto a rotating 99.99%-pure ZnO target, with $n$-type Si (001) substrates positioned at a distance of 50 mm. Deposition was conducted for 20 min, which grew ZnO nanohemisphere arrays with a thickness of approximately 20 nm, measured by a calibrated quartz crystal thickness monitor.

To produce a wide variety of surface morphologies, hence $\text{SVR}$ values, the 12 thin-films underwent further processing, namely 6 samples by thermal annealing and 6 samples by chemical etching. Annealing was performed in Ar gas from 573 to 1073 K, in 100 K intervals. The etched samples were first annealed at 873 K in Ar gas, then etched in HCl, diluted with H$_2$O to a pH of 2.16, at different etching temperatures from 273 to 333 K in 10 K intervals. To prevent the HCl from unintentionally modifying the barrier height, samples were rinsed thoroughly with deionized water and immediate dried in nitrogen gas after the etching process.
Subsequent to post-processing, Schottky (Pt) and ohmic (Ti/Pt) contacts were deposited onto the samples through a stainless steel shadow mask at 200 °C. The sputtering power was set to 100 W. The average thickness of the metal contacts was calibrated by a quartz crystal microbalance. 99.99% (Sigma Aldrich) pure Ti and Pt sputtering targets were used. The base pressure of the chamber was $6.7 \times 10^{-5}$ mbar and the working pressure using pure Ar gas was maintained at $6.7 \times 10^{-3}$ mbar. Fig. 1 depicts the structure of the fabricated Pt/ZnO Schottky barrier based on a nanohemisphere array. The 12 samples were then characterized in terms of $I-V$ characteristic and surface morphology. $I-V$ characteristics were obtained by wire bonding the electrodes and measuring with a Keithley 2400 sourcemeter at temperatures between 273 to 473 K in 50 K increments. Characterization by AFM (Veeco Instruments) was performed prior to the deposition of the Schottky contact at room temperature.

**RESULTS AND DISCUSSION**

Fig. 3 and Fig. 4 respectively show the $I-V$ characteristics of differently annealed (A1-A6) and etched (E1-E6) samples. It is evident that surface morphology changes across annealing temperature and etching conditions. Specifically, the distribution of nano-hemisphere geometries for ZnO samples annealed at different temperatures can be seen as Gaussian. Annealing at 800 °C shows the largest radius, broadest radius distribution and the highest hemisphere height, which suggest that nanograins coalesce uniformly with respect to increasing annealing temperature. This is consistent with previous reports. As for the effect of etching conditions, the surface roughness of the ZnO film increases with the HCl concentration, time and temperature, which is consistent with previous reports. In Fig. 3 and Fig. 4, the value of $I_S$ for Eq. (14) can be obtained from the well-known method of projecting the forward biased current onto the y-axis. To estimate the SVR, Eq. (14) is evaluated. For the annealed samples A1-A6, the evaluated SVR values are 0.35, 0.45, 0.55, 0.46, 0.58 and 0.65 nm$^{-1}$, respectively. For the etched samples E1-E6, the evaluated SVR values are 7.14, 3.14, 4.68, 5.97, 6.99 and 7.14 nm$^{-1}$, respectively. In the evaluation of Eq. (14), $N_D$ has been obtained by Hall Effect measurement. Approaches such as C-V measurements are also common for obtaining $N_D$. Other well-established parameters such as $\Phi_M$, $\chi_{SC}$ and $\varepsilon_S$ can be obtained from well-established references.

For a quantitative comparison, the surface morphologies of the 12 samples were characterized by AFM. Fig. 5 and Fig. 6 depict 3D surface scans of the annealed (A1-A6) and etched (E1-E6) samples, respectively. The measured SVR values are, for A1-A6, 0.69, 0.54, 0.51, 0.52, 0.47 and 0.32 nm$^{-1}$, and for E1-E6, 7.09, 6.22, 5.68, 4.12, 3.32 and 2.36 nm$^{-1}$, respectively.

**FIG. 3.** $I-V$ characteristics of Pt/ZnO nanohemisphere Schottky interfaces prepared by post-annealing from 573 to 1073 K in 100 K intervals. The $I-V$ data is measured from 273 K to 473 K, at 50 K intervals between -1 to 1V bias voltages. The samples are denoted S1 to S6.
FIG. 4. I-V characteristics of the Pt/ZnO nanohemisphere Schottky interfaces prepared by etching in HCl diluted to pH of 2.16 at 273 to 333 K in 10 K intervals. The I-V data is measured from 273 K to 573 K, at 50 K intervals between -1 to 1V bias voltages. The samples are denoted E1 to E6.

Table I summarizes the above comparison in terms of percentage error, which is in all cases within a few percents, suggesting the proposed technique is capable of achieving high accuracy. In general, the SVR obtained by the proposed technique matches measurement closely, indicating

FIG. 5. AFM surface scans of samples S1-S6. SVR values are (a) 0.69, (b) 0.54, (c) 0.51, (d) 0.52, (e) 0.47 and (f) 0.32 nm$^{-1}$.

FIG. 6. AFM surface scans of samples E1-E6. SVR values are (a) 7.09, (b) 6.22, (c) 5.68, (d) 4.12, (e) 3.32 and (f) 2.36 nm$^{-1}$.
that it is an effective approach for SVR estimation via I-V characteristics for nanohemisphere based Schottky barriers.

CONCLUSION

In this work, we present a surface area to volume ratio (SVR) estimation technique based on I-V measurements, for nanohemisphere based metal-semiconductor (Schottky) barriers. By rooting our formulation on Gauss’s law, i.e. without deviating from first principles, we have expanded classical thermionic emission theory to incorporate surface area and volume. The proposed technique has been assessed by comparison against AFM measured surface characteristics from 12 fabricated Pt/ZnO nanostructured thin-films. Results show that the proposed estimation technique has a high accuracy of within several percents from actual measurements, which offer access to surface morphology characterization of nanostructures using simple I-V measurements.

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1 P. Reddy, B. Sarkar, F. Kaess, M. Gerhold, E. Kohn, R. Collazo, and Z. Sitar, *Applied Physics Letters* **110**, 011603 (2017).
2 A. Di Bartolomeo, *Physics Reports* **606**, 1 (2016).
3 E. Comini, *Materials Today* **19**, 559 (2016).
4 X. Wang, M. Zhao, H. Li, Y. Song, and S. Chen, *Electrochimica Acta* **249**, 173 (2017).
5 S. M. Sze, *Semiconductor devices: physics and technology* (John Wiley & Sons, 2008).
6 B. Sharma, *Metal-semiconductor Schottky barrier junctions and their applications* (Springer Science & Business Media, 2013).
7 R. T. Tung, *Applied Physics Reviews* **1**, 011304 (2014).
8 D. Navarro, F. Herrera, H. Zenitani, M. Miura-Mattausch, N. Yorino, H. J. Mattausch, M. Takusagawa, J. Kobayashi, and M. Harada, *Japanese Journal of Applied Physics* **57**, 04FR03 (2018).
9 C. A. de Amorim, E. P. Bernardo, E. R. Leite, and A. J. Chiquito, *Semiconductor Science and Technology* (2018).
10 G. Smit, S. Rogge, and T. Klapwijk, *Applied Physics Letters* **81**, 3852 (2002).
11 A. Szymczak, M. Wisło, T. Szymański, and R. Paszkiewicz, *Ultramicroscopy* **170**, 77 (2016).
12 M. Drygas and J. F. Janik, *Materials Chemistry and Physics* **133**, 932 (2012).
13 T. Düren, F. Millange, G. Férey, K. S. Walton, and R. Q. Snurr, *The Journal of Physical Chemistry C* **111**, 15350 (2007).
14 S. Mohan, V. Kumar, D. K. Singh, and S. H. Hasan, *Journal of Environmental Chemical Engineering* **5**, 2259 (2017).
15 W. Yu, K. Sephrnoori, and T. W. Patzek, *SPE Journal* **21**, 589 (2016).
16 J. R. Rumble and J. Rumble, *CRC Handbook of Chemistry and Physics*, 98th Edition (CRC Press LLC, 2017).
17 G. M. Valnalme, L. Goubert, R. L. Van Meirhaeghe, F. Cardon, and P. Van Daele, “A ballistic electron emission microscopy study of barrier height inhomogeneities introduced in Au/III-V semiconductor Schottky barriers contacts by chemical pretreatments,” *Semicond. Sci. Technol.* **14**, 871–877 (1999).
18 Y. C. Chan, J. Yu, and D. Ho, “Morphology, stoichiometry, and crystal structure control via post-annealing in Pt – ZnO nanograin Schottky barriers interfaces,” *Applied Surface Science* **443**, 506–514 (2018).
19 Y. C. Lin, Y. C. Jian, and J. H. Jiang, “A study on the wet etching behavior of AZO (ZnO: Al) transparent conducting film,” Applied Surface Science 254, 2671–2677 (2008).
20 S.-C. Her and T.-C. Chi, “Optical and electrical performance of ZnO films textured by chemical etching,” Material Sciences 21, 502–505 (2015).
21 S. K. Cheung and N. W. Cheung, Applied Physics Letters 49, 85 (1986).