## Substrate-diamond interface considerations for enhanced thermionic electron emission from nitrogen doped diamond films

Cite as: J. Appl. Phys. **112**, 113707 (2012); https://doi.org/10.1063/1.4766442 Submitted: 30 August 2012 • Accepted: 20 October 2012 • Published Online: 06 December 2012

Franz A. M. Koeck and Robert J. Nemanich

### ARTICLES YOU MAY BE INTERESTED IN

Combined visible light photo-emission and low temperature thermionic emission from nitrogen doped diamond films

View Onli

Applied Physics Letters 99, 202101 (2011); https://doi.org/10.1063/1.3658638

Synthesis and characterization of highly-conducting nitrogen-doped ultrananocrystalline diamond films

Applied Physics Letters 79, 1441 (2001); https://doi.org/10.1063/1.1400761

Optimal emitter-collector gap for thermionic energy converters Applied Physics Letters **100**, 173904 (2012); https://doi.org/10.1063/1.4707379





J. Appl. Phys. 112, 113707 (2012); https://doi.org/10.1063/1.4766442

 $\ensuremath{\textcircled{}^{\circ}}$  2012 American Institute of Physics.



# Substrate-diamond interface considerations for enhanced thermionic electron emission from nitrogen doped diamond films

Franz A. M. Koeck and Robert J. Nemanich

Department of Physics, Arizona State University, Tempe, Arizona 85287-1504, USA

(Received 30 August 2012; accepted 20 October 2012; published online 6 December 2012)

Thermionic electron emission from low work function doped diamond films can be related to materials' properties, which include donor states, surface electron affinity, and substrate-diamond interface properties. The focus of this study is on how the properties of the substrate material affect the emission. Two aspects are considered, the substrate electrical resistance and the substrate Richardson constant, and the effects of tungsten, molybdenum and rhenium substrates are explored. Low work function diamond films were deposited on the substrates, and the thermionic emission was measured to ~530 °C and described in terms of a fit to the Richardson-Dushman formalism. The results establish that all surfaces exhibit a similar work function but the Richardson constant and maximum emission current vary considerably. The rhenium based emitter displayed a low work function of 1.34 eV, a significant Richardson constant of  $53.1 \text{ A/cm}^2 \text{ K}^2$ , and an emission current density of ~44 mA/cm<sup>2</sup> at a temperature of  $530 \degree$ C. The results indicated that interface carbide formation could limit the emission presumably because of increased electrical resistance. For non-carbide forming substrates, an increased substrate Richardson constant corresponded to enhanced emission from the diamond based emitter. @ 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4766442]

#### I. INTRODUCTION

Efficient electron sources find applicability in devices for high power telecommunications, space propulsion, and direct thermal to electrical energy conversion.<sup>1–5</sup> In many systems, the emitter operating temperature is determined by the required electron emission current density which is governed by material parameters for thermionic emission, the emission barrier or work function, and emission or Richardson's constant. The work function of a material is dependent on the electronic states at the surface while a range of properties contribute to the Richardson's constant which determines the emission current at a specific temperature. Conventional materials employed in thermionic emitter applications, e.g., refractory metals such as tungsten and molybdenum, are characterized by a high work function of 4.5 eV and 4.1 eV, and high values for Richardson's constant of  $74 \text{ A/cm}^2 \text{ K}^2$  and  $55 \text{ A/cm}^2 \text{ K}^2$ , respectively. These Richardson's constants approach the theoretical value of  $120 \text{ A/cm}^2 \text{ K}^2$ . For practical devices, work function lowering techniques are required to extract suitable emission currents. This includes application of cesium at the emitter surface which reduces the work function to values of about 1.3 eV. However, a significant reduction in the Richardson constant to  $\sim 3 \text{ A/cm}^2 \text{ K}^2$  has been observed for Cs adsorbed on refractory metal surfaces.<sup>6</sup> This lowering in the emission constant was attributed to a temperature coefficient of the work function greater than that for clean metals, or to a greater degree of reflection of electrons at the metal surface.<sup>7</sup>

While thermionic electron emission from metal based emitters has been well established, ongoing interest in diamond based electron sources can be attributed to two key material properties: the ability of diamond surfaces to gain negative electron affinity (NEA) properties, and the ability of its crystal lattice to accept donor atoms. In our previous research, doping by phosphorus and nitrogen resulted in low work function thermionic emitters where we reported a work function of 0.9 eV for phosphorus doped diamond thin films prepared on molybdenum.<sup>8</sup> However, emission was observed to be limited by a reduced value of the Richardson's constant  $(10 \,\mu\text{A/cm}^2 \text{ K}^2)$  which was attributed to increased film resistivity. In a different study, nitrogen doped diamond emitter resistivity was controlled by utilizing a low resistivity nitrogenincorporated ultra nanocrystalline diamond (N)UNCD interstitial layer where we measured a low work function of 1.29 eV and a larger Richardson constant of 0.84 A/cm<sup>2</sup> K<sup>2.8</sup> Recently, Paxton et al. prepared similar nitrogen-incorporated polycrystalline diamond films on molybdenum substrates for a thermionic emission study and reported a work function of 2.22 eV and a Richardson's constant of 5.96 A/cm<sup>2</sup> K<sup>2.9</sup> This increased value of Richardson's constant was attributed in part to reduced film resistivity and more complete hydrogen termination providing a higher density of low work function surface sites for emission. For nanocrystalline diamond films, Uppireddi et al. have reported a work function of about 3.3 eV which was observed to increase to about 4.4 eV at 900 °C.<sup>10</sup> This increase in the work function can be attributed to a loss of NEA properties at elevated temperatures. Typical values for the electron affinity of various diamond surfaces have been reported to be  $\sim -1.1 \text{ eV}$ .<sup>11,12</sup> Results have shown that vacuum annealing of a nanocrystalline surface at  $\sim$ 1100 °C reverts its NEA to a positive value of about  $+0.2 \,\mathrm{eV.}^{13}$  For oxygen terminated surfaces, a positive electron affinity can be induced with a reported value of 1.7 eV.<sup>14</sup>

As electron transport occurs across the structure, this study investigates how the substrate-diamond interface properties effectuate thermionic emission of the device. We will evaluate thermionic emission in terms of substrate resistivity and Richardson's constant for three metal substrates: molybdenum, tungsten, and rhenium. Distinct values of these parameters have been reported for the metals and their carbides which are presented in Table I. The range of values for the Richardson's constant was reported for various crystallographic faces of the respective single crystal metal. The Richardson's constant for rhenium is close to the theoretical value of 120 A/cm<sup>2</sup> K<sup>2</sup>. In the absence of literature data and with the low solubility of carbon in rhenium, the theoretical value for the emission constant for Re + C was assumed.

Furthermore, we will establish whether a Schottkybarrier can be expected at the back contact and whether it presents a substantial effect to thermionic electron emission. As diamond deposition occurs at elevated temperatures interface carbide formation will be addressed, and its contribution to thermionic emission will be described in terms of resistivity and Richardson's constant. While tungsten and molybdenum exhibit interface carbide formation, rhenium, a high Richardson constant material, does not display carbide formation. Our results will establish whether thermionic electron emission is more advantageously effected by a change in resistivity or the value of Richardson's constant.

#### II. EXPERIMENTAL

The base substrate materials for diamond deposition were 1 in. diameter disks of 99.95% purity molybdenum, tungsten, and molybdenum/rhenium alloy with 47.5% rhenium content. In order to promote diamond nucleation, the roughness of the metal substrate surface was controlled by a bead blasting procedure. For pure rhenium surfaces, a molybdenum substrate surface was sputter etched to remove any native oxide which was followed by evaporation of 99.99% rhenium with a final film thickness of 5 nm. Prior to diamond deposition, the metal substrate surface was sonicated in a nanodiamond suspension, rinsed with acetone, and dried with nitrogen gas. This procedure provided nucleation enhancement for diamond film growth. The emitter structure, prepared by plasma assisted chemical vapor deposition, was comprised of a nitrogen incorporated ultra-nanocrystalline diamond, (N)UNCD, layer and a thin nitrogen-doped diamond top layer. The (N)UNCD layer was synthesized under addition of 10 sccm argon, 20 sccm methane, and 100 sccm nitrogen. Microwave power was adjusted to 900W at a chamber pressure of 20 Torr and a substrate temperature of  $\sim 900$  °C. The nitrogen-doped diamond top layer was prepared by shutting off the argon flow, establishing the hydrogen flow at 400 sccm and reducing the methane flow to 2 sccm with concurrent increase of microwave power to 1300 W and chamber pressure to 50 Torr. The final diamond film surface was exposed to a pure hydrogen plasma to induce negative electron affinity properties.

Thermionic electron emission measurements were conducted in a UHV system with a base pressure  $<2 \times 10^{-10}$ Torr. The diamond emitter was mounted on a radiatively heated sample stage, and an optical pyrometer was employed to control sample temperature. In the measurement configuration, the emitter and collector were separated by a 50  $\mu$ m thick BN spacer and a bias of 20 V was applied to collect emitted electrons. This applied field is not sufficient to cause field emission. The emitter was held at electrical ground and an electrical contact was made to the collector *in vacuo* by a moveable actuator. Thermionic electron emission was recorded with a Keithley 2400-LV source-measurement unit.

The electron emission current density, J(T), was recorded as a function of emitter temperature, and analyzed with respect to the Richardson–Dushman formalism (1) allowing extraction of the work function  $\varphi$  and Richardson constant A<sub>R</sub> by a fitting procedure. The current density J(T) was fit to the following expression:

$$J(T) = A_R T^2 e^{-\frac{\varphi}{k_B T}},\tag{1}$$

where

$$A_R = CF \cdot A_0, \tag{2}$$

with a correction factor (CF) which varies with material parameters and temperature and

$$A_0 = \frac{4\pi m_e k_B^2 k e^2}{h},\tag{3}$$

the theoretical value of Richardson's constant  $(120 \text{ A/cm}^2 \text{ K}^2)$  with Boltzmann's constant, k<sub>B</sub>, electron mass, m<sub>e</sub>, electronic charge, e, and Planck's constant, h.<sup>22</sup>

#### **III. RESULTS AND DISCUSSION**

This study begins with the evaluation of thermionic electron emission of a doped diamond emitter structure prepared on a molybdenum substrate as presented in Figure 1. From a data fit to the Richardson formalism, a low work function of 1.42 eV can be deduced. This reduced emission

TABLE I. Work function  $\varphi$ , emission constant A<sub>R</sub>, and resistivity  $\rho$  for various metals and their carbides used in thermionic emitter applications. Resistivity values are presented for a temperature of 500 °C.<sup>20,21</sup>

Material	Work function $\varphi$ (eV)	Richardson $A_R$ (A/cm <sup>2</sup> K <sup>2</sup> )	Resistivity $\rho \ (\mu \Omega \ cm)$	Carbide	Work function $\varphi$ (eV)	Resistivity $\rho$ ( $\Omega$ cm)	$\begin{array}{c} \text{Richardson } A_{R} \\ (A/cm^{2}  K^{2}) \end{array}$
Molybdenum	4.15	38–39 (Refs. 15 and 16)	17.5	Mo <sub>2</sub> C	3.7	130	23
Tungsten	4.54	55-104 (Ref. 17)	19	WC	3.6	2	96
Rhenium	4.7	110-320 (Ref. 18)	52	Re + C	4.1	52	120
Cesium	1.81	162 (Ref. 19)					
Cs on W	1.36	3.2					
BaO + SrO	0.95	$\sim 10^{-2}$					

barrier was attributed in part to decreased band bending at the surface due to the nano-structured film morphology and the propagation of states from the (N)UNCD layer into the top nitrogen doped diamond film. The data fit also indicates a Richardson constant of 0.69 A/cm<sup>2</sup> K<sup>2</sup>. Suzuki et al. prepared similar films with nitrogen concentration of  $2.7 \times 10^{20}$  cm<sup>-3</sup> on silicon and reported a work function of 1.99 eV with a Richardson constant of about 70 A/cm<sup>2</sup> K<sup>2</sup>.<sup>23</sup> The same group measured a saturation current of 1.4 mA at  $670 \,^{\circ}\text{C}$  from a  $14 \,\text{mm} \times 14 \,\text{mm}$  substrate. It should be noted that diamond deposition on silicon results in a 1-10 nm SiC layer.<sup>24</sup> Richardson constants for Si and SiC have been reported as 112 A/cm<sup>2</sup> K<sup>2</sup> and 72 A/cm<sup>2</sup> K<sup>2</sup>, respectively.<sup>25,26</sup> A comparison with these results and noting the electrical resistance values in Table I suggests that the interstitial Mo<sub>2</sub>C layer in the device structure as well as the resistivity of the nitrogen-doped diamond layer can limit the value of the Richardson's constant. It should be stated that data that exhibit a higher degree of deviation from the law of Richardson-Dushman could be described by an alternate set of work function and Richardson's constant. In this case, a higher work function would coincide with a higher value for Richardson's constant.

In successive experiments, a similar nitrogen doped diamond structure was synthesized on tungsten and a molybdenum/rhenium alloy. For tungsten with resistivity of  $19 \mu\Omega$ cm at 500 °C, an emission constant of 80 A/cm<sup>2</sup> K<sup>2</sup> has been measured. Its carbide resistivity has been reported to be  $\sim 2 \mu \Omega$  cm at a temperature of 500 °C with a slightly increased Richardson constant of 96 A/cm<sup>2</sup> K<sup>2</sup>.<sup>27</sup> The molybdenum/rhenium alloy can be characterized by a resistivity of  $40 \,\mu\Omega$  cm at a temperature of 500 °C, significantly higher than its tungsten-carbide counterpart and the additional benefit of a non carbide forming rhenium phase. Table I details resistivity and Richardson's constant for molybdenum carbide and tungsten carbide. Comparing molybdenum carbide and tungsten carbide indicates a reduction in resistivity by a factor of 65 while the value of Richardson's constant is increased by a factor of  $\sim 4$ .



FIG. 1. Thermionic electron emission from nitrogen doped diamond structures prepared on various substrate materials.

An emitter structure grown on tungsten versus molybdenum results in enhanced emission characterized by an increased value of Richardson's constant by a factor of  $\sim 2$ . This indicates that the value of the substrate's Richardson's constant presents a more advantageous contribution to thermionic emission than a decrease in resistivity.

Evaluation of thermionic electron emission from doped diamond on a molybdenum/rhenium substrate as shown in Figure 1 presents significant enhancement in the emission current density, which may be related to an increased value of Richardson's constant of the alloy. In a different study, tungsten/rhenium alloys with varying rhenium concentration were investigated with respect to thermionic emission properties. For tungsten samples with 2% and 6% rhenium a Richardson constant of  $110 \text{ A/cm}^2 \text{ K}^2$  and  $130 \text{ A/cm}^2 \text{ K}^2$ , respectively, was measured.<sup>28</sup> The same report has attempted to analyze the value of Richardson's constant in terms of a reflection coefficient of the form  $\alpha \exp(-p^2/2m\omega)$ , where  $\alpha$ and  $\omega$  are constants and p is the component of the normal momentum outside the surface. It was suggested that with accurate knowledge of the emitter temperature,  $\alpha$  and  $\omega$ could then be determined, and predictions could be provided for the value of A<sub>R</sub>.

During the initial exposure step in diamond film growth, surface reactions between the substrate and the active gas species can result in a thin layer of amorphous carbon, metal carbide, or graphite. The properties of the intermediate layer is determined by the substrate material and the thickness affected by carbon interdiffusion. During diamond deposition, the molybdenum surface will react to form a carbide, Mo<sub>2</sub>C, with a reported thickness of  $1.5-3 \,\mu m.^{29,30}$  With a Richardson constant of  $A_R = 23 \,\text{A/cm}^2 \,\text{K}^2$  for Mo<sub>2</sub>C, a significant reduction from the metallic value of 55  $\text{A/cm}^2 \,\text{K}^2$  is observed.<sup>31</sup> At a temperature of 500 °C, the electrical resistivity of molybdenum has been measured as 17.5  $\mu\Omega$  cm and its carbide resistivity is 130  $\mu\Omega$  cm.

Electron supply from the substrate necessitates examination of the metal-diamond electrical contact. Utilization of an n-type nitrogen incorporated UNCD interstitial layer in the device structure suggests the absence of a Schottky barrier at the substrate-diamond interface due to the high nitrogen incorporation and due to the graphitic grain boundaries.<sup>32</sup> In fact, it has been reported that metal contacts to ntype UNCD films are typically ohmic in nature; independent of the metal work function.<sup>33</sup> As the thermionic emission current is affected by device resistivity, the interface electrical resistance of the emitter layer structure may limit the emission. Various metal contacts on doped nanocrystalline diamond have shown an electrical contact resistance in the range of  $10^{-5}$ – $10^{-7} \Omega$  cm, about 2 orders of magnitude smaller than contacts prepared on undoped films. This observation suggests a negligible contribution to electrical device resistance from the ohmic contact at the metallic substratediamond interface.

To further investigate the role of rhenium at the substrate-diamond interface, a pure rhenium layer was evaporated onto a clean molybdenum substrate, and an optimized doped diamond emitter structure was synthesized on the rhenium film. This optimization included adjustment of the



FIG. 2. Thermionic electron emission from an optimized nitrogen doped diamond structure deposited on a rhenium thin film.

thicknesses of the (N)UNCD and N-doped diamond layers. Thermionic electron emission was evaluated in vacuum with respect to the Richardson-Dushman formalism with results presented in Figure 2.

Similar to previous emitter results (Figure 1), a low work function of ~1.3 eV can be extracted from the data fit. The enhanced emission current is reflected in the Richardson's constant which increased to a value of 53.1 A/cm<sup>2</sup> K<sup>2</sup>. This emitter sustained a significant emission current density of ~44 mA/cm<sup>2</sup> at a temperature of 530 °C. In contrast to the other refractory metals used in this report, rhenium exhibits the highest electrical resistivity of about 52  $\mu\Omega$  cm at a temperature of 500 °C. This suggests that for increased emission a higher resistivity of the substrate can be offset by a higher value of Richardson's constant.

In a summary comparison, Figure 3 depicts the observed relation between thermionic electron emission current from a nitrogen doped diamond film at 500 °C and its metallic substrates resistivity and Richardson's constant. From the plot in Figure 3, it can be deduced that thermionic electron emission from a nitrogen doped diamond film is enhanced by a substrate material which exhibits a larger Richardson's constant, i.e., rhenium. The main contribution to the emission current enhancement is then not determined by the substrate electrical resistance.

Operation at elevated temperatures requires a stable substrate-diamond interface and thus necessitates evaluation of rhenium-carbon interactions. Reports indicate low solubility of carbon in rhenium (less than 1% w/w) with no significant carbide formation.<sup>34</sup> Furthermore, rhenium contacts on carbon rich 6H-SiC surfaces have been shown to be stable at temperatures of 1000 °C with undetectable interface reaction.<sup>35</sup>

#### **IV. CONCLUSION**

We have prepared a layered structure of nitrogen incorporated ultra-nanocrystalline diamond with a nitrogen doped diamond top layer on various substrate materials for thermionic emission characterization. The focus of this research was the substrate-diamond interface and its effects on thermionic electron emission, in particular, on its corresponding value of Richardson's constant. Refractory metals like molybdenum and tungsten, typically employed in thermionic emitter devices, form interface layers, mainly carbides, due to the carbon rich ambient in diamond growth. These interstitial layers may limit emission current density due to increased resistivity and reduced Richardson's constant. Rhenium interstitial layers, which do not form carbides and exhibit low carbon solubility, provide enhanced thermionic emission from a deposited nitrogen doped diamond emitter, which was attributed to the increased value of Richardson's constant for rhenium and its stable interface. While rhenium exhibits higher resistivity its increased value of Richardson's constant offsets the current limiting parameter and our results indicate a significant effect on the Richardson's constant of the final doped-diamond emitter structure.



FIG. 3. Thermionic electron emission current at 500 °C from nitrogen doped diamond films prepared on Mo, W, and Re substrates and the Richardson's constants and resistivity values.

#### ACKNOWLEDGMENTS

This research was supported by the Office of Naval Research.

- <sup>1</sup>V. L. Granatstein, Proc. IEEE 87, 702 (1999).
- <sup>2</sup>P. J. Wilbur, IEEE Trans. Plasma Sci. **19**, 1167 (1991).
- <sup>3</sup>S. M. Merkowitz, P. G. Maghami, A. Sharma, W. D. Willis, and C. M. Zakrzwski, Class. Quantum Grav. **19**, 1745 (2002).
- <sup>4</sup>J. L. Van Noord, H. Kamhawi, and H. K. McEwen, in *The 29th International Electric Propulsion Conference*, IEPC-2005-321, Princeton, NJ, 2005.
- <sup>5</sup>P. Shefsiek, IEEE Trans. Plasma Sci. 38, 2041 (2010).
- <sup>6</sup>W. Kohl, *Handbook of Materials and Techniques for Vacuum Devices* (American Institute of Physics, New York, 1967).
- <sup>7</sup>D. A. Wright, in *Proceedings of the IEE Part III: Radio and Communication Engineering*, Vol. 100, No. 65, pp. 125–139, May 1953, doi: 10.1049/ pi-3.1953.0030.
- <sup>8</sup>F. A. M. Koeck and R. J. Nemanich, Diamond Relat. Mater. 18, 232 (2009).
- <sup>9</sup>W. F. Paxton, M. Howell, W. P. Kang, and J. L. Davidson, J. Vac. Sci. Technol. B **30**, 021202 (2012).
- <sup>10</sup>K. Uppireddi, T. L. Westover, T. S. Fisher, B. R. Weiner, and G. Morel, J. Appl. Phys. **106**, 043716 (2009).
- <sup>11</sup>F. Maier, J. Ristein, and L. Ley, Phys. Rev. B **64**, 165411 (2001).
- <sup>12</sup>J. B. Cui, J. Ristein, and L. Ley, Phys. Rev. Lett. **81**, 429 (1998).
- <sup>13</sup>B. M. Nichols, J. E. Butler, J. N. Russell, Jr., and R. J. Hamers, J. Phys. Chem. B 109, 20938 (2005).
- <sup>14</sup>M. Tachiki, Y. Kaibara, Y. Sumikawa, M. Shigeno, H. Kanazawa, T. Banno, K. S. Song, H. Umezawa, and H. Kawarada, Surf. Sci. 581, 207 (2005).
- <sup>15</sup>R. C. Jaklevic and D. W. Juenker, J. Appl. Phys. **33**, 562 (1962).
- <sup>16</sup>F. M. Gardner, F. E. Girouard, W. L. Boeck, and E. A. Coomes, Surf. Sci. 26, 605 (1971).

- <sup>17</sup>G. F. Smith, Phys. Rev. 100, 1115 (1955).
- <sup>18</sup>A. Kashetov and N. A. Gorbatyi, Sov. Phys. J. 12, 856 (1969).
- <sup>19</sup>V. S. Fomenko, *Handbook of Thermionic Properties* (Plenum, New York, 1966).
- <sup>20</sup>R. O. Jenkins, Vacuum **19**, 353 (1969).
- <sup>21</sup>P. G. Pallmer, R. L. Gordon, and M. J. Dresser, J. Appl. Phys. **51**, 3776 (1980).
- <sup>22</sup>O. W. Richardson, Phys. Rev. 23, 153 (1924).
- <sup>23</sup>M. Suzuki, T. Ono, N. Sakuma, and T. Sakai, Diamond Relat. Mater. 18, 1274 (2009).
- <sup>24</sup>B. R. Stoner, G. -H. M. Ma, S. D. Wolter, and J. T. Glass, Phys. Rev. B 45, 11067 (1992).
- <sup>25</sup>J. Huran, in *The Fourth International Conference on Advanced Semiconduc*tor Devices and Microsystems (IEEE, 2002), p. 67, doi: 10.1109/ASDAM. 2002.1088476.
- <sup>26</sup>J. P. Henning, K. J. Schoen, M. R. Melloch, J. M. Woodall, and J. A. Cooper, J. Electron. Mater. 27, 296 (1998).
- <sup>27</sup>M. Liao, Y. Koide, and J. Alvarez, J. Vac. Sci. Technol. B 24, 185 (2006).
- <sup>28</sup>A. E. Abey, J. Appl. Phys. **39**, 120 (1968).
- <sup>29</sup>P. Bou, L. Vandenbulcke, R. Herbin, and F. Hillion, J. Mater. Res. 7, 2151 (1992).
- <sup>30</sup>R. Meilunas, M. S. Wong, K. C. Sheng, R. P. H. Chang, and R. P. Van-Duyne, Appl. Phys. Lett. **54**, 2204 (1989).
- <sup>31</sup>J. H. Ingold, J. Appl. Phys. **34**, 2033 (1963).
- <sup>32</sup>J. E. Gerbi1, O. Auciello, J. Birrell, D. M. Gruen, B. W. Alphenaar, and J. A. Carlisle, Appl. Phys. Lett. 83, 2001 (2003).
- <sup>33</sup>O. A. Williams, Semicond. Sci. Technol. **21**, R49 (2006).
- <sup>34</sup>M. Ritschel, A. Leonhardt, D. Elefant, S. Oswald, and B. Büchner, J. Phys. Chem. C 111, 8414 (2007).
- <sup>35</sup>G. Y. McDaniel, S. T. Fenstermaker, W. V. Lampert, and P. H. Holloway, J. Appl. Phys. 96, 5357 (2004).