Ni/Si solid phase reaction studied by temperature-dependent current-voltage technique

Yu-Long Jiang and Guo-Ping Ru[a]
Department of Microelectronics, ASIC & System State Key Laboratory, Fudan University, Shanghai 200433, China

Fang Lu
State Key Laboratory of Applied Surface Physics, Fudan University, Shanghai 200433, China

Xin-Ping Qu and Bing-Zong Li
Department of Microelectronics, ASIC & System State Key Laboratory, Fudan University, Shanghai 200433, China

Simon Yang
Technology Development Center, Semiconductor Manufacturing International Corporation, 18 Zhangjiang Road, Shanghai 201203, China

(Received 29 May 2002; accepted 17 October 2002)

The temperature-dependent current–voltage ($I-V-T$) technique has been used to study the Ni/Si solid phase reaction by measuring the Schottky barrier height (SBH) inhomogeneity of Ni-silicide/Si Schottky diodes. The experimental results show the strong dependence of SBH inhomogeneity on the Ni/Si solid phase reaction. The SBH distribution of the diodes annealed at 500 and 600 °C can be described by a single-Gaussian function and the diode annealed at 500 °C is found to have the best homogeneity and the smallest leakage current. The SBH distribution of the diodes annealed at 400, 700, and 800 °C can be described by a double-Gaussian function in which the mean value of the second Gaussian function is substantially smaller than that of the dominant Gaussian function. The variation of SBH inhomogeneity, an interface property, is related to the phase evolution process in the Ni/Si solid phase reaction, and verified by reverse $I-V$ measurements. Our results indicate that the $I-V-T$ technique may be developed as a wafer-level testing tool to monitor the silicidation process in the complementary metal–oxide–semiconductor device fabrication. [DOI: 10.1063/1.1527714]

I. INTRODUCTION

Self-aligned silicides (salicides) have been a key component of high-performance complementary metal–oxide–semiconductor (CMOS) devices for several technology nodes.[1–3] For the commonly used silicides such as $TiSi_2$ and $CoSi_2$, it is well known that the resistivity of $TiSi_2$ increases rapidly as the linewidth scales down to the sub-quarter-micron regime because of the difficulty of phase transition from C54 to C49,[4,5] and $CoSi_2$ is more sensitive to the scaling of junction depth and can exhibit high leakage on shallow junctions.[2,3,6–8] Both silicides need significant Si consumption to achieve a low sheet resistance, which is in contradiction with the scaling down tendency of junction depth. Recently, NiSi was demonstrated to be a promising salicide candidate for sub-0.1 μm CMOS devices,[9–13] even for so-claimed 30 nm physical gate length CMOS transistors.[14] Solid phase reaction of Ni/Si is one of the key issues for Ni-salicide technology, for example, the annealing temperature for NiSi formation should be optimized when it is implemented in CMOS fabrication. Many material characterization techniques such as x-ray diffraction, Auger electron spectroscopy, Rutherford backscattering spectroscopy, and Raman scattering spectroscopy have been used to investigate the Ni/Si solid phase reaction. However, there are some limits on these techniques. First, some of them can only be applied to large area samples, and there is evidence that the properties of large area samples may be different from those of patterned samples with small geometry. For example, the formation of the $NiSi_2$ phase may take place at as low as 400 °C on small holes and narrow lines on patterned Si (111).[15] Second, signals obtained by all those material characterization techniques are proportional to the volume or area percentage of certain phases or atoms. But a very small amount of some defects at or close to the silicide/Si interface which cannot be easily detected by those techniques may have strong influence on salicide device characteristics. In the meanwhile, a Schottky diode is the most sensitive device to detect the defects or other imperfections at or close to the silicide/Si interface and there are few reports on the electronic properties of a Ni-silicide/Si interface formed by solid phase reaction, though there are some reports on the $I-V$ characteristics and the leakage mechanism of Ni-silicided *pn* junctions.[16] In this article the temperature-dependent current–voltage ($I-V-T$) technique is used to investigate the Ni/Si solid phase reaction by measuring the Schottky barrier height (SBH) inhomogeneity of Ni-silicide/Si contacts.

[a]Electronic mail: gpru@fudan.edu.cn

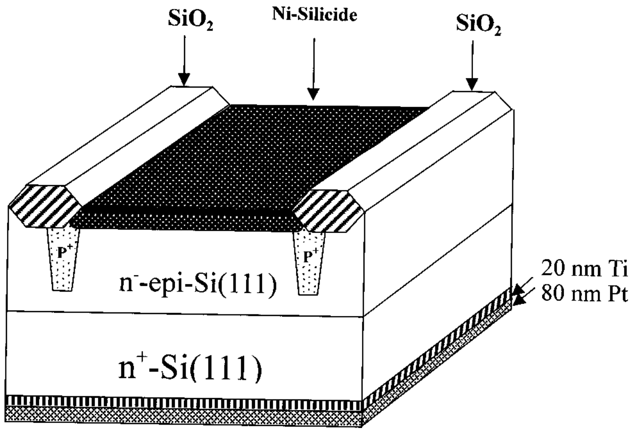

FIG. 1. Final structure of the patterned samples. There is a boron-diffused guard ring to eliminate edge effects in the Schottky diode.

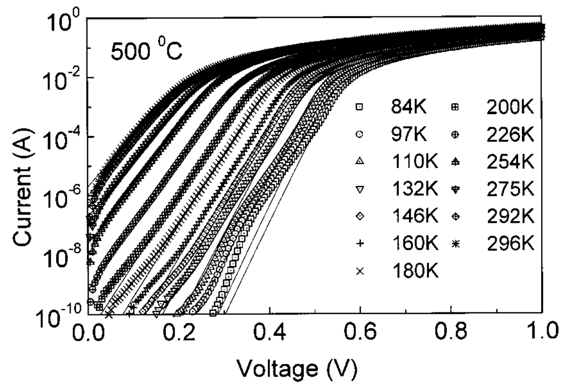

FIG. 3. $I-V-T$ curves of the Ni-silicide/n-Si Schottky diode formed at 500 °C.

II. EXPERIMENT

A 20 nm Ni film was deposited on patterned and blanket n-epi (5–8 Ω cm)/n^+-Si(111) substrates by Ar^+ beam sputtering, which were cleaned by a RCA procedure prior to Ni deposition. The patterned substrate has a number of contact holes (0.78×0.78 mm^2) protected by a boron-diffused guard-ring. The silicidation process was carried out *ex situ* by rapid thermal annealing (RTA) in a dry nitrogen ambient at temperature from 300 to 1000 °C for 2 min. For patterned substrates, the unreacted metals were etched in a boiling H_2SO_4:H_2O_2=4:1 solution. After silicide formation, 20 nm Ti film and 80 nm Pt film were sequentially deposited on the backside of the patterned samples to form the ohmic contact. The final structure of the patterned samples is shown in Fig. 1. A linear four-point probe was used to measure the sheet resistance of the blanket substrates. For the patterned samples, $I-V-T$ measurement was carried out using a Keithley 2400 sourcemeter and a Keithley 2700 multimeter/data acquisition system controlled by a computer in a cryostat. The measurement temperature ranges from 78 to 299 K.

III. RESULTS AND DISCUSSION

Figure 2 shows the dependence of sheet resistance of Ni-silicide film on annealing temperature. The samples annealed at 400, 500, 600, 700, and 800 °C were selected to carry out $I-V-T$ measurements due to their low sheet resistance and all these Ni-silicide/n-Si Schottky diodes show a rectifying characteristic. Figure 3 shows the $I-V$ curves of the sample annealed at 500 °C at various measuring temperatures. The current across an ideal Schottky diode at a forward bias V_a, based on the thermionic emission theory, is given by the following relation when $V_a > 3kT/q$:[17]

$$I(V_a) = A_d A^{**} T^2 \exp\left(-\frac{\phi}{kT}\right) \exp\left[\frac{q(V_a - IR_s)}{nkT}\right], \qquad (1)$$

where A_d is the diode area, A^{**} is the effective Richardson constant of Si (about 112 A cm^{-2} K^{-2} for Si), T is the temperature in Kelvin, k is the Boltzmann constant, q is the electronic charge, ϕ is the barrier height in eV, n is the ideality factor, and R_s is the series resistance of the diode. When the SBH is not homogeneous the $I-V$ characteristics can still be expressed by Eq. (1), except that the ϕ is replaced by an apparent barrier height ϕ_{ap}. For example, for an inhomogeneous Schottky contact with a Gaussian distribution of SBH, the apparent barrier height can be expressed as[18,19]

$$\phi_{ap} = \overline{\phi} - \frac{\sigma^2}{2kT}, \qquad (2)$$

where $\overline{\phi}$, σ are the mean value and the standard deviation of the Gaussian function. The solid lines in Fig. 3 are fitting curves according to Eq. (1) by taking ϕ_{ap}, n, R_s as fitting parameters. Figure 4 shows the ϕ_{ap}-$1/T$ relationship of all the measured diodes. From the figure one can see that ϕ_{ap} decreases linearly with the increase of the inverse of temperature for samples annealed at 500 and 600 °C, indicating that the SBH inhomogeneity can be well described by a single-Gaussian distribution function [Eq. (2)] and the fitting results are shown as the two straight lines in the figure according to Eq. (2). For samples annealed at other temperatures, the ϕ_{ap}-$1/T$ relation deviates from the linear law, indicating that a more complicated distribution function has to be used to describe the SBH inhomogeneity.[20] It is found that the SBH inhomogeneity can be described by a double distribution (double-Gaussian[20] or Gaussian and lognormal[21]). For an inhomogeneous Schottky diode with a double-Gaussian distribution of barrier height, the apparent barrier height can be expressed as[20]

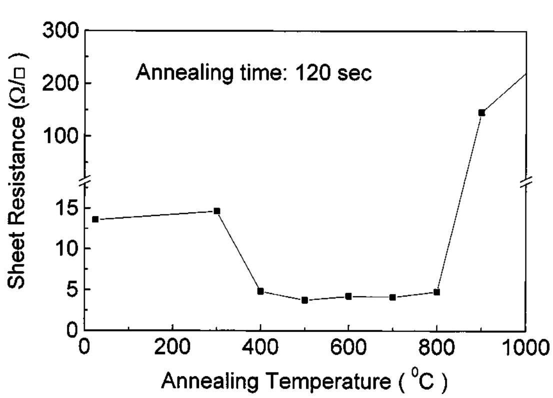

FIG. 2. Dependence of sheet resistance of Ni-silicide film on annealing temperature of a Ni/Si solid phase reaction.

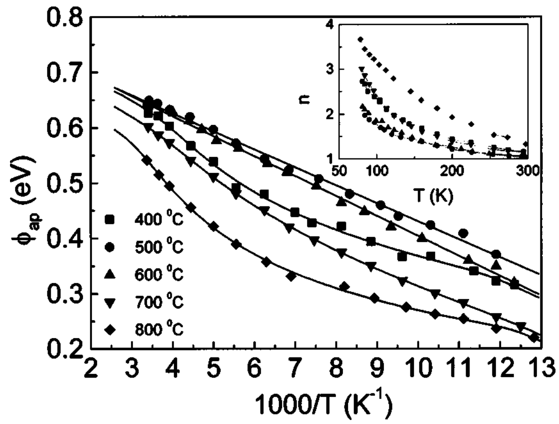

FIG. 4. ϕ_{ap}-$1/T$ relationship of all the measured Ni-silicide/*n*-Si diodes. The inset shows the temperature dependence of ideality factor.

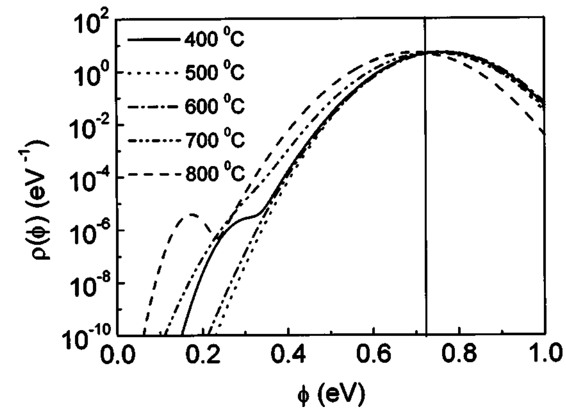

FIG. 5. SBH distribution of all the Ni-silicide/*n*-Si contacts.

$$\phi_{ap} = -kT \ln\left[\rho_1 \exp\left(-\frac{\overline{\phi}_1}{kT} + \frac{\sigma_1^2}{2k^2T^2}\right) + \rho_2 \exp\left(-\frac{\overline{\phi}_2}{kT} + \frac{\sigma_2^2}{2k^2T^2}\right)\right], \tag{3}$$

where ρ_1, ρ_2 ($\rho_2 = 1-\rho_1$), σ_1, σ_2, and $\overline{\phi}_1$, $\overline{\phi}_2$ are the weight, standard deviation, and mean value of two Gaussian functions, respectively. The solid lines in Fig. 4 are fitting curves according to Eq. (3) by taking ρ_1, ρ_2 ($\rho_2 = 1-\rho_1$), σ_1, σ_2, and $\overline{\phi}_1$, $\overline{\phi}_2$ as fitting parameters. All the extracted parameters of each measured diode are listed in Table I. According to these parameters the barrier height distribution function $\rho(\phi)$ of all the diodes can be obtained.

Figure 5 shows the dependence of SBH inhomogeneity on Ni/Si annealing temperature. At $\phi = 0.72$ eV, all the $\rho(\phi)$ have the same probability. For ϕ lower than 0.72 eV, the distribution of $\rho(\phi)$ for the Ni-silicide/*n*-Si contact formed at different temperature follows such a law, i.e., $\rho(\phi)(500\,°C) < \rho(\phi)\ (600\,°C) < \rho(\phi)(400\,°C) < \rho(\phi)(700\,°C) < \rho(\phi)\ (800\,°C)$. Combining the consideration of the importance of the low SBH patches with the actual distribution of $\rho(\phi)$ in Fig. 5, we can directly draw the conclusion that the apparent barrier height follows the same law, i.e., $\phi_{ap}(500\,°C) > \phi_{ap}(600\,°C) > \phi_{ap}(400\,°C) > \phi_{ap}(700\,°C) > \phi_{ap}(800\,°C)$, as shown in Fig. 4.

The ideality factor, especially its temperature dependence, sometimes can also be an indicator of SBH inhomogeneity.[22] The relationship of the extracted ideality factor n versus measurement temperature T is shown in the inset of Fig. 4. From the inset it is easy to see that with the decreasing of measurement temperature the extracted ideality factors of all the samples increase, which is in agreement with most other reports on inhomogeneous Schottky contact.[19,22,23] Furthermore, there is a trend that $n(500\,°C) < n(600\,°C) < n(400\,°C) < n(700\,°C) < n(800\,°C)$ at low temperature range (less than 150 K) where it is the low SBH patches that play an important role. According to the analysis of Dobročka *et al.*, SBH inhomogeneity may result in a temperature-dependent ideality factor and the larger the inhomogeneity, the higher the ideality factor.[22] So we can deduce the same trend of SBH inhomogeneity from the ideality factor for all the samples as that obtained by the analysis of the ϕ_{ap}-$1/T$ relationship. However, sometimes the temperature dependence of an ideality factor can also be related to the thermionic-field emission (TFE) of carriers across the metal–semiconductor interface.[17] The characteristic energy for tunneling can be expressed as[17]

$$E_{00} = 18.5 \times 10^{-15}\left(\frac{N_d}{\varepsilon_r m_n^*/m_0}\right)^{1/2} \text{eV}, \tag{4}$$

where ε_r, m_n^*, m_0, and N_d are the relative permittivity of the semiconductor material, effective mass of electron, mass of free electron, and density of dopant in m^{-3}, respectively. In our experiment, $N_d \approx 10^{21}\ m^{-3}$, then $E_{00} \approx 0.19$ meV. According to the theory of TFE it will dominate only when $E_{00} \approx kT$ and the value of E_{00} calculated from Eq. (4) is far less than kT, even at 77 K. Therefore tunneling should be insignificant in our experiments. Moreover, with guard-rings, the edge effects of a Schottky diode, which are the possible causes for the enhancement of TFE,[24] should be suppressed to a minimum level.

The variation of SBH inhomogeneity with silicidation temperature can be related to the Ni/Si solid phase reaction. Generally, a Ni/Si solid phase reaction goes through the following stages: $Ni/Si \rightarrow Ni_2Si \rightarrow NiSi \rightarrow NiSi_2$.[25] At 400 °C the resultant film contains mainly NiSi grains and a small amount of Ni_2Si grains whose resistivity is larger than that of NiSi, which results in a larger sheet resistance of the film than that of pure NiSi film as shown in Fig. 2. Because of the incomplete and inhomogeneous diffusion process of Ni atoms into Si to form the more stable phase NiSi, the interface

TABLE I. . Extracted parameters ρ_1, ρ_2 ($\rho_2 = 1-\rho_1$), $\overline{\phi}_1$, $\overline{\phi}_2$, and σ_1, σ_2 of all the measured diodes.

	ρ_1	ρ_2	$\overline{\phi}_1$ (eV)	$\overline{\phi}_2$ (eV)	σ_1 (eV)	σ_2 (eV)
400 °C	2.15×10^{-7}	$1-\rho_1$	0.305	0.760	0.0345	0.0789
500 °C	1	0	0.756		0.0749	
600 °C	1	0	0.766		0.0789	
700 °C	8.94×10^{-6}	$1-\rho_1$	0.412	0.742	0.0584	0.0827
800 °C	2.38×10^{-7}	$1-\rho_1$	0.174	0.696	0.0247	0.0800

of Ni-silicide/Si is rough and then there are relatively many nonideal patch contacts with low barrier height due to various contact structures, which causes the second Gaussian distribution below $\phi = 0.35$ eV as shown in Fig. 5. At 500 °C the resultant film is pure NiSi whose resistivity is the smallest as shown in Fig. 2. At this stage the film is the most stable and the NiSi/Si interface is the smoothest and the most homogeneous. The patches with lower SBH are the least. The second Gaussian distribution below $\phi = 0.35$ eV formed at 400 °C disappears in this sample as shown in Fig. 5. The distribution of $\rho(\phi)$ is also the most commonly observed single-Gaussian function. At 600 °C the interface becomes a little rougher due to the beginning of phase transition of $NiSi \rightarrow NiSi_2$, which also causes the sheet resistance of film to slightly increase as shown in Fig. 2 due to the higher resistivity of $NiSi_2$. The distribution $\rho(\phi)$ is globally left-shifted comparing with that of 500 °C, which correspondingly leads to the distribution of ϕ_{ap} versus $1/T$ globally lower than that of 500 °C as shown in Fig. 4. The standard deviation σ is also larger than that of 500 °C. At 700 °C the stable $NiSi_2$ forms. However, the excessive stress due to the epitaxial tendency of $NiSi_2$ grains on Si may greatly change the $NiSi_2$/Si contact structure.[25] Again the nonideal patches with extremely low barrier height significantly form, which leads to the presence of the second Gaussian distribution as shown in Table I. The distribution $\rho(\phi)$ is further globally left- shifted compared to that of 600 °C, leading to the distribution of ϕ_{ap} versus $1/T$ further globally lower than that of 600 °C as shown in Fig. 4. At 800 °C the $NiSi_2$ film starts to agglomerate. During such high temperature annealing significant interdiffusion of Ni and Si atoms occurs and the $NiSi_2$ film may groove and island. As can be seen in Fig. 2, 800 °C is the beginning point of rapid increase of the sheet resistance. The degradation of the film causes the roughest Ni-silicide/Si contact interface, which results in the second Gaussian distribution function whose mean value is further lower than that of 700 °C as shown in Fig. 5. The distribution $\rho(\phi)$ is further globally left-shifted compared to that of 700 °C, correspondingly leading to the globally lowest distribution of ϕ_{ap} versus $1/T$ as shown in Fig. 4.

To further evaluate the quality of the silicide/Si interface, the reverse $I-V$ characteristics of Ni-silicide/*n*-Si contacts have been measured. The deep-level transient spectroscopy measurements of all these samples do not detect any deep levels, indicating that the reverse current should not contain much generation current of defects. The contribution of small low SBH patches to total current across a diode may be suppressed by large spreading resistance under forward bias, but they may have very important influence on the reverse current of the Schottky diode according to Eq. (1). The more the low SBH patches in a diode, the higher the reverse current. The experimental results show that $I_r(500\,°C) < I_r(600\,°C) < I_r(400\,°C) < I_r(700\,°C) < I_r(800\,°C)$, where I_r is the reverse current of each diode. The result is in good agreement with the strong dependence of SBH inhomogeneity on the annealing temperature for Ni-silicide formation.

IV. CONCLUSION

In summary, the $I-V-T$ technique has been used to study the Ni/Si solid phase reaction by measuring the SBH inhomogeneity of Ni-silicide/Si Schottky diodes. The conventional single-Gaussian distribution function or the double-Gaussian distribution function is successfully used to describe the SBH inhomogeneity of all the diodes. The experimental results reveal the strong dependence of SBH inhomogeneity on Ni/Si solid phase reaction temperature. The diodes annealed at 500 and 600 °C can be described by a single-Gaussian distribution function and the diode annealed at 500 °C is found to have the best homogeneity and the least leakage current. The diodes annealed at 400, 700, and 800 °C can be described by a double-Gaussian distribution function whose mean value of the second Gaussian function is substantially smaller than that of the dominant one. Since the electrical characteristics of the silicide/Si Schottky contact is very sensitive to defects or other imperfections at or close to the silicide/Si interface, the SBH inhomogeneity may be used as a measure to evaluate the silicide/Si interface quality. The results obtained in this work indicate that the $I-V-T$ technique may be developed as a wafer-level testing tool to monitor silicidation processing in the CMOS device fabrication.

ACKNOWLEDGMENTS

This work was supported by Natural Science Foundation of China (NSFC- 60106002), Shuguang project from Shanghai Municipal Education Commission and Shanghai Education Development Foundation, and Doctoral Foundation from Ministry of Education of China.

[1] K. Maex, Mater. Sci. Eng., R. **11**, 53 (1993).
[2] J. A. Kittl and Q. Z. Hong, Thin Solid Films **320**, 110 (1998).
[3] J. A. Kittl, Q. Z. Hong, H. Yang, N. Yu, S. B. Samavedam, and M. A. Gribelyuk, Thin Solid Films **332**, 404 (1998).
[4] J. B. Lasky, J. S. Nakos, O. J. Cain, and P. J. Geiss, IEEE Trans. Electron Devices **38**, 262 (1991).
[5] J. A. Kittl, D. A. Prinslow, P. P. Apte, and M. F. Pas, Appl. Phys. Lett. **67**, 2308 (1995).
[6] K. I. Goto, J. Watanabe, T. Sukegawa, A. Fushida, T. Sakuma, and T. Sugii, Proceedings of the 36th Annual International Reliability Physics Symposium, 1998, p. 363.
[7] Q. Z. Hong, W. T. Shiau, H. Yang, J. A. Kittl, C. P. Chao, H. L. Tsai, S. Krishnan, I. C. Chen, and R. H. Havemann, Tech. Dig. Int. Electron Devices Meet. **1997**, 107.
[8] K. Goto, I. Fushida, J. Watanabe, T. Sukegawa, K. Kawamura, T. Yamazaki, and T. Sugii, Tech. Dig. Int. Electron Devices Meet. **1995**, 449.
[9] T. Morimoto, T. Ohguro, H. S. Momose, T. Iinuma, I. Kunishima, K. Suguro, I. Katakabe, H. Nakajima, M. Tsuchiaki, M. Ono, Y. Katsumata, and H. Iwai, IEEE Trans. Electron Devices **42**, 915 (1995).
[10] D. X. Xu, S. R. Das, J. P. McCaffrey, C. J. Peters, and L. E. Erickson, Mater. Res. Soc. Symp. Proc. **402**, 59 (1996).
[11] E. G. Colgan, J. P. Gambino, and B. Cunningham, Mater. Chem. Phys. **46**, 209 (1996).
[12] Q. Z. Hong, S. Q. Hong, F. M. D'Heurle, and J. M. E. Harper, Thin Solid Films **23**, 479 (1994).
[13] J. Chen, J. P. Colinge, D. Flandre, R. Gillon, J. P. Raskin, and D. Vanhoenacker, J. Electrochem. Soc. **144**, 242 (1997).
[14] R. Chau, J. Kavalieros, B. Roberds, R. Schenker, D. Lionberger, D. Barlage, B. Doyle, R. Arghavani, A. Murthy, and G. Dewey, Tech. Dig. Int. Electron Devices Meet. **2000**, 45.

[15] J. Y. Yew, L. J. Chen, and K. Nakamura, Appl. Phys. Lett. **69**, 999 (1996).
[16] D. Z. Chi, D. Mangelinck, S. K. Lahiri, P. S. Lee, and K. L. Pey, Appl. Phys. Lett. **78**, 3256 (2001).
[17] E. H. Rhoderick and R. H. Williams, *Metal-Semiconductor Contacts*, 2nd ed. (Clarendon, Oxford, 1988).
[18] Y. P. Song, R. L. Van Meirhaeghe, W. H. Laflere, and F. Cardon, Solid-State Electron. **29**, 633 (1986).
[19] J. H. Werner and H. H. Guttler, J. Appl. Phys. **69**, 522 (1991).
[20] Y.-L. Jiang, G.-P. Ru, F. Lu, X.-P. Qu, B.-Z. Li, W. Li, and A.-Z. Li, Chin. Phys. Lett. **19**, 553 (2002).
[21] Zs. J. Horváth, Vacuum **46**, 963 (1995).
[22] E. Dobročka and J. Osvald, Appl. Phys. Lett. **65**, 575 (1994).
[23] R. T. Tung, Phys. Rev. B **45**, 13509 (1992).
[24] S. Hardikar, M. K. Hudait, P. Modak, S. B. Krupanidhi, and N. Padha, Appl. Phys. A: Mater. Sci. Process. **68**, 49 (1999).
[25] F. D'Heurle, J. Mater. Res. **71**, 3812 (1992).