JOURNAL OF APPLIED PHYSICS VOLUME 84, NUMBER 9 1 NOVEMBER 1998

Temperature dependence of the barrier height of Pt/*n*-GaAs Schottky diodes

H.-W. Hübers[a] and H. P. Röser
German Aerospace Center (DLR), Institute of Space Sensor Technology, Rudower Chaussee 5, 12489 Berlin, Germany

(Received 26 February 1998; accepted for publication 27 July 1998)

The dependence on temperature of the Schottky barrier height of Pt on *n*-GaAs is reported. Two different behaviors are observed. The Schottky contacts of one group have a mean barrier height of 1.018 eV and a temperature coefficient of −0.23 meV/K while the contacts of the other group have a significantly lower barrier height of 0.922 eV which is almost independent of the temperature. These results are interpreted on the basis of recent models of Fermi level pinning. While the Fermi level in the diodes of the first group is pinned to a charge neutrality level, it is pinned by defects in the diodes of the second group. © *1998 American Institute of Physics.* [S0021-8979(98)02021-0]

I. INTRODUCTION

Metal–semiconductor or so called Schottky contacts are rectifying and mixing. Due to these properties they have found a wealth of applications. In this article we report on the electrical characteristics of Pt/*n*-GaAs Schottky diodes. These diodes are frequently used as mixers in low noise heterodyne receivers for the frequency range from 500 GHz up to 5 THz. Such receivers have high sensitivity, high spectral resolution, and a large instantaneous bandwidth which makes them an important tool in radio astronomy, remote sensing of the atmosphere and plasma diagnostics.[1] A wealth of molecules and atoms have transitions which fall in the THz frequency region. Very often they can only be detected at these frequencies. One prominent example is the OH radical which is a major catalytic substance in the stratosphere and troposphere. Only recently OH has been detected for the first time with an airborne heterodyne receiver with a Pt/*n*-GaAs Schottky diode as the mixing element.[2] Other examples for THz heterodyne receivers with Pt/*n*-GaAs Schottky diodes are the instruments aboard the ODIN and the SWAS satellites.[3,4] With these instruments the earth's stratosphere as well as weak astronomical sources will be observed in the frequency range from 500 to 600 GHz. Pt/*n*-GaAs diodes are also used in micromachined integrated components for THz frequencies.[5] Since the sensitivity of a THz heterodyne receiver is determined by the Schottky diode mixer a detailed understanding of the underlying physical mechanism is of major importance in order to improve the performance of the whole spectrometer.

Besides these important applications Pt/*n*-GaAs Schottky diodes are also interesting from the viewpoint of fundamental research. During the past few years it has been shown that Pt/*n*-GaAs Schottky diodes work as mixers up to 30 THz well above their cutoff frequency of 2–10 THz which is determined by their series resistance and capacitance.[6] In addition, mesoscopic effects seem to play an important role in the conduction and mixing mechanism of submicron Pt/*n*-GaAs Schottky diodes.[7,8]

Of prime interest in a metal–semiconductor system is the formation of the potential barrier. Its height is determined by the position of the Fermi level within the semiconductor band gap. In general the exact position of the Fermi level depends on the details of the interface. At a perfect, defect free interface the barrier height is determined by the charge neutrality level of the metal induced gap states (MIGS). These states originate from the tails of the metal wave functions into the semiconductor. Close to the valence band maximum they are predominantly donor-like while close to the conduction band minimum they are predominantly acceptor-like. The cross over between both types is called the charge neutrality level. Charge neutrality requires the alignment of this level with the Fermi level of the metal and therefore determines the barrier height. This model does not account for any chemical reactions or imperfections at the interface. Fabrication induced interface defects can exist in addition to the MIGS and alter the barrier height. The defects give rise to additional discrete levels in the band gap and the Fermi level is pinned to one of these levels, possibly quite far away from the charge neutrality level.

The dependence of the Schottky barrier height on temperature can give insight into the physical mechanism of the Fermi level pinning in a certain metal semiconductor contact. When the Fermi level is pinned to the charge neutrality level, the temperature dependence of the barrier height is governed by the temperature dependence of the band gap, the direct gap as well as the indirect gap.[9,10] However, if the Fermi level is pinned by defects their ionization entropy would control the temperature dependence of the barrier height.[11] Since the temperature dependence of the ionization entropy is much smaller than that of the energy gap, measurements of the temperature evolution allow one to distinguish between both pinning mechanisms.

In the course of this study we have investigated the barrier heights of Pt/*n*-GaAs Schottky diodes and their temperature dependence. All diodes are commercially available and are used as mixers in low noise THz heterodyne receivers.

[a]Electronic mail: heinz-wilhelm.huebers@dlr.de

TABLE I. Parameters of the investigated Schottky diodes.

Diode	Manufacturer	Epitaxial layer	Ohmic backcontact	Doping density (10^{17} cm^{-3})	Reference
SDO 20	Farran Technology	MBE	SnNi/Au	0.5	16
DA499	TU Darmstadt	MBE	Ni/AuGe/Ni	1.0	17
HSD3S	Tohoku University	MBE	Ni/AuGe	1.0	13
1T6	Univ. of Virginia (UVa)	MOCVD	SnNi/Ni/Au	1.0	18
1I7 a	UVa	MBE	SnNi/Ni/Au	3.0	18
1I7 b	UVa	MBE	SnNi/Ni/Au	3.0	18
1I7 c	UVa	MBE	SnNi/Ni/Au	3.0	18
1T12	UVa	MOCVD	SnNi/Ni/Au	3.0	18
1I12	UVa	MBE	SnNi/Ni/Au	4.5	18
1T14	UVa	MOCVD	SnNi/Ni/Au	10.0	19
1T15	UVa	MOCVD	SnNi/Ni/Au	10.0	19

The results are interpreted on the basis of recent models of Schottky barrier formation and Fermi level pinning. The role played by MIGS and interface defects in this process is discussed.

II. EXPERIMENTAL SETUP

The Schottky contact of all diodes is a submicron-size dot of Pt on a GaAs (100) epitaxial layer. Depending on the diode the epitaxial layer is either grown by molecular beam epitaxy or by metalorganic chemical vapor deposition on top of an n^+-GaAs substrate with a doping density of about 5×10^{18} cm^{-3}. The thickness and the doping of the epitaxial layers vary between 300 and 1000 Å and 10^{16}–10^{18} cm^{-3}, respectively. The dopant is silicon. Immediately prior to the anode formation the uppermost GaAs layers were etched away with an oxide etch in order to yield a high quality and nearly stoichiometric surface.[12,13] Afterwards Pt was deposited by electrochemical plating. This method is known to produce less defects at the Pt–GaAs interface and a larger barrier than thermal evaporation of the metal onto the semiconductor.[14,15] On the backside of the substrate an ohmic contact of either SnNi/Ni/Au, Ni/AuGe, or Ni/AuGe/Ni is deposited. For details of the manufacturing process see Refs. 13, 16–19. All relevant data about the investigated Schottky diodes are listed in Table I.

The current–voltage ($I-V$) curves were measured at temperatures varying from 300 to 80 K. Cooling was performed with a closed cycle He refrigerator. The temperature was measured with a Si temperature diode mounted close to the Schottky contact. In order to make sure that the temperature of the Schottky diode under investigation is the same as the temperature measured by the Si diode a delay of 15 min between two measurements was kept. This procedure was checked by replacing the Schottky diode with a Si temperature diode and measuring the temperature with both Si diodes. The difference in the measured temperature between the two Si diodes was always less than 0.1 K. The temperature could be held constant within ±0.1 K by the use of a stabilization loop. The loop consisted of the temperature diode, a heating resistance and a Lake Shore temperature controller, which regulates the temperature to a preset value. All measurements were performed in the dark. The voltage was supplied by a Keithley 236 voltage source which simultaneously measured the current.

As an example, the $I-V$ curves of the Schottky diode 1I7 c at different temperatures are plotted in Fig. 1. For clarity they are shown only for a few temperatures between 80 and 300 K. As one can see the $I-V$ curves shift to higher bias voltages and are getting steeper with decreasing temperature. It is worth noting that they are linear over several orders of magnitude.

III. METHOD OF ANALYSIS

When the current flow through a Schottky contact can be described by a thermionic emission theory the $I-V$ relationship of a Schottky diode is given by

$$I=I_S \exp(qV/nkT)[1-\exp(-qV/kT)]. \quad (1)$$

Here q is the electronic charge, k is Boltzmann's constant, T is the temperature, V is the applied forward voltage, and n is the empirical ideality coefficient. I_S is the saturation current given by

$$I_S=A^{**}ST^2 \exp(-q\Phi_{b0}/kT), \quad (2)$$

where A^{**} is the effective Richardson constant taken as 8.6×10^4 A m^{-2} K^{-2}, S is the anode area, and Φ_{b0} is the zero-bias barrier height. We have performed least squares fits of Eq. (1) to the linear part of the measured $I-V$ curves. From these fits n and I_S were determined. Once I_S is known, the zero-bias barrier height can be easily computed with the

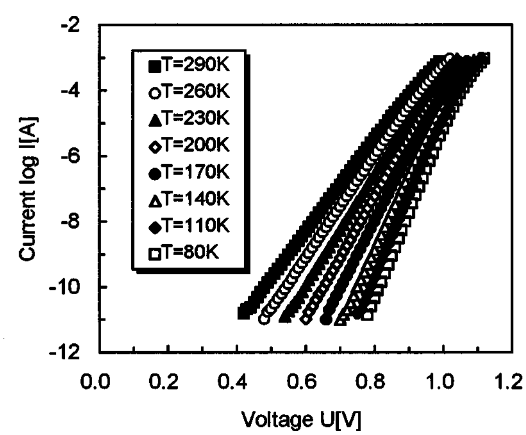

FIG. 1. $I-V$ characteristics of the Schottky diode 1I7 c as a function of temperature.

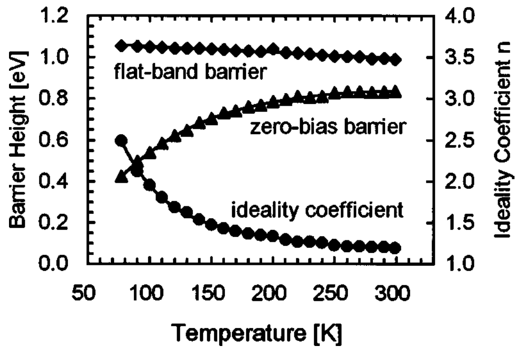

FIG. 2. Ideality coefficient, zero-bias barrier height and flatband barrier height as a function of temperature for the Schottky diode 1I7 c. While the zero-bias barrier height increases with temperature the flatband barrier height decreases slightly.

help of Eq. (2). Figure 2 shows the results for the diode 1I7 c. While the ideality coefficient decreases with temperature the zero-bias barrier height increases.

The barrier height of a Schottky diode depends on the electric field across the contact and consequently on the applied bias voltage. In order to compare different Schottky contacts it is therefore necessary to specify standard field conditions. It has been shown previously[20,21] that the flatband barrier height is the fundamental barrier height which should be used when comparing experiments with theory. Under this condition the semiconductor bands are flat, which precludes tunneling and image force lowering from affecting the $I-V$ characteristic. The flatband barrier height can be calculated from the ideality coefficient and the zero-bias barrier height according to[20]

$$\Phi_{\mathrm{bf}}=n\Phi_{b0}-(n-1)(kT/q)\ln(N_C/N_D), \tag{3}$$

where Φ_{bf} is the flatband barrier height, N_C is the effective density of states in the conduction band, and N_D is the ionized donor density. Both, N_C and N_D, are functions of the temperature. This is taken into account in our analysis. It is worth noting that the flatband barrier height is independent of the current transport mechanism. Therefore it can be determined also for highly doped diodes where tunneling contributes significantly to the total current resulting in an ideality coefficient larger than 1. In fact, analysis of the flatband barrier height has been performed up to $n=3$ (Ref. 22). From theoretical considerations[20] as well as from experiments[21] it can be concluded that the flatband barrier height is essentially the same as the barrier height determined by the capacitance–voltage ($C-V$) method.

The flatband barrier height has been determined for a variety of metal/semiconductor combinations. In particular, Chin, Green, and Storey have performed an extended study of metal/GaAs systems.[21] However, no measurements of Pt/n-GaAs contacts have been performed by this method.

IV. TEMPERATURE DEPENDENCE OF THE BARRIER HEIGHT

The temperature dependence of the flatband barrier height in the range from 80 to 300 K can be expressed as

$$\Phi_{\mathrm{bf}}(T)=\Phi_{\mathrm{bf}}(T=0\ \mathrm{K})+\alpha T, \tag{4}$$

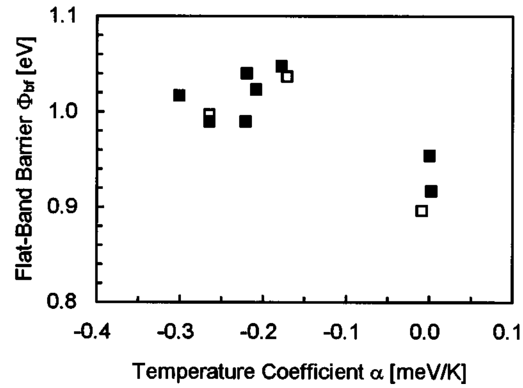

FIG. 3. Flatband barrier height as a function of the temperature coefficient for all investigated Schottky diodes. One can clearly distinguish two groups; one with a high barrier and strong temperature dependence and the other with a significantly smaller barrier height which is almost independent of temperature. The open rectangular symbols belong to the diodes 1I7 a, 1I7 b, and 1I7 c which are nominally the same (see Table I). It is worth noting that these diodes can also belong to the two different groups.

where $\Phi_{\mathrm{bf}}(T=0\ \mathrm{K})$ is the flatband barrier height extrapolated to zero temperature and α is its temperature coefficient. The numerical values of α for all Schottky diodes are given in Table II together with the flatband barrier height, the zero-bias barrier height, and the ideality coefficient (all at 300 K).

For a further analysis the flatband barrier height is plotted as a function of the temperature coefficient (Fig. 3). From this plot it is obvious that the Schottky contacts split into two groups. For group 1 contacts, the temperature coefficient varies between -0.17 and -0.30 meV/K with a mean value of -0.23 ± 0.02 meV/K while the flatband barrier height is 1.018 ± 0.008 eV. The latter value compares very well with previous $C-V$ measurements of Pt/n-GaAs contacts [$\Phi_b=1.00\pm0.03$ eV (Ref. 23)] showing once more that both methods yield the same results. In contrast, the contacts of group 2 have a mean temperature coefficient of -0.002 ± 0.004 meV/K and a barrier height of 0.922 ± 0.021 eV. These values are significantly lower than the ones for group 1 Schottky contacts. It is worth noting that even diodes which are nominally the same can belong to the two different

TABLE II. Measured ideality coefficients, zero-bias barrier heights, flatband barrier heights (all at 300 K) and temperature coefficients of the Schottky diodes.

Diode	Ideality coefficient n	Zero-bias barrier height Φ_{b0} (eV)	Flatband barrier height Φ_{bf} (eV)	Temperature coefficient α (meV/K)
SDO 20	1.28	0.830	1.048	−0.18
DA499	1.12	0.917	1.017	−0.30
HSD3S	1.16	0.827	0.954	0.00
1T6	1.39	0.758	1.040	−0.22
1I7 a	1.16	0.780	0.896	−0.01
1I7 b	1.34	0.777	1.037	−0.17
1I7 c	1.20	0.836	0.997	−0.27
1T12	1.22	0.821	0.990	−0.22
1I12	1.23	0.833	1.023	−0.21
1T14	1.67	0.544	0.917	0.02
1T15	1.57	0.628	0.990	−0.27

groups. An example is the diode 1I7. While diode 1I7 a belongs to group 2, the diodes 1I7 b and 1I7 c belong to group 1 (see Table II and Fig. 3).

The results of the group 1 Schottky contacts can be interpreted on the basis of the model developed by Tersoff.[9,10] There it is assumed that the Fermi level is pinned in the center of the band gap which is at or near the charge neutrality level. It identifies the relevant gap center with the center of the minimum indirect gap. Instead of the actual valence band maximum E_V its position in the absence of spin–orbit splitting is considered. Therefore the relevant gap center is given by

$$E_0=\tfrac{1}{2}(E_V^*+E_C^i), \tag{5}$$

where $E_V^*=E_V-\Delta/3$ is the valence band maximum in the absence of spin–orbit splitting Δ, and E_C^i is the indirect conduction band minimum. In order to account for the dependence of the barrier height on the metal an adjustable parameter δ_m is introduced, allowing for a shift of the Fermi level from the gap center E_0. Taking this into account the barrier height of p-type material is given by

$$\Phi_{\text{bp}}=\tfrac{1}{2}(E_g^i-\Delta/3)+\delta_m. \tag{6}$$

Here E_g^i is the minimum indirect band gap of the semiconductor [1.71 eV for GaAs at 300 K (Ref. 24)] and Δ is the spin–orbit splitting [0.34 eV for GaAs (Ref. 24)]. For metal–GaAs contacts, as for most Schottky contacts, the barrier heights on p-type and on n-type material add up to the energy gap, i.e., $E_g=\Phi_{\text{bp}}+\Phi_{\text{bn}}$ (Ref. 15) [$E_g=1.42$ eV at 300 K (Ref. 24)]. Therefore the barrier height on n-GaAs is given by

$$\Phi_{\text{bn}}=E_g-\tfrac{1}{2}(E_g^i-\Delta/3)-\delta_m. \tag{7}$$

According to Eq. (5) the temperature dependence of the barrier height is controlled by the variation of the direct and the indirect band gap:

$$d\Phi_{\text{bn}}/dT=dE_g/dT-\tfrac{1}{2}dE_g^i/dT. \tag{8}$$

The linearized temperature dependence of the direct energy gap is -0.39 meV/K (Ref. 24) while for the indirect gap it is -0.43 meV (Ref. 24). From this a temperature coefficient of -0.18 meV/K for the barrier height is expected. Our measurements are in good agreement with this result. The determination of δ_{Pt} yields -0.40 eV. This is smaller than the average value for gold on different semiconductors which is -0.2 eV (Ref. 9). However, for the Au/GaAs system $\delta_{\text{Au}}=-0.33$ eV which is the largest deviation from the average value of all investigated contacts in Ref. 10. δ_{Pt} should be smaller than δ_{Au} because Pt is more electronegative than Au considering the electronegative values as determined by Miedema (in Ref. 15).

The close to zero temperature coefficients of the group 2 Schottky barriers mean that for these contacts the Fermi level is pinned by interface defects or imperfections at the metal–semiconductor interface. Revva *et al.*[11] pointed out that if the Fermi level is pinned by defects the barrier height of an n-type semiconductor changes only weakly with temperature because their ionization entropy changes only weakly with temperature. This would explain our result for the group 2 Schottky contacts. In addition, positively charged interface defects reduce the barrier height of metals on n-type semiconductors. According to Mönch[15] the maximum reduction of the barrier height $\delta\Phi_B$ for a metal on n-GaAs is given by

$$\delta\Phi_B\approx N_I/D_{\text{MIGS}}, \tag{9}$$

where N_I is the density of interface states and D_{MIGS} is the density of metal induced gap states. This tacitly assumes that all defects are charged. For the diodes of group 2 the reduction of the barrier height is about 0.1 eV and $D_{\text{MIGS}}\approx3.7\times10^{14}\ \text{eV}^{-1}\,\text{cm}^{-2}$ (Ref. 15) yielding $N_I\approx3.7\times10^{13}\ \text{cm}^{-2}$. This is about one fiftieth of the total density of sites in GaAs (100) planes. Ho *et al.*[25] investigated the barriers of NiSi/Si systems. According to their findings, imperfections at the interface of only a minute can lower the barrier height by about 10% to 15% in agreement with our results.

It has been shown that the oxide etch of the GaAs prior to the anode formation yields a slightly nonstoichiometric surface with excess As.[12,13] The magnitude of this excess can vary from one to another fabrication run. Thus, missing Ga atoms which act as donors will dominate the Fermi level pinning provided the As excess is big enough. Defects due to missing Ga atoms give rise to an energy level of 0.55 ± 0.10 eV above the valence band maximum.[26] Pinning of the Fermi level at this energy results in a barrier height of 0.87 ± 0.10 eV in agreement with the barrier height measured for the group 2 diodes. The missing Ga atoms are not necessarily simple vacancies but can be As atoms at Ga sites or even more complicated such as PtGa complexes which are known to form at the Pt/GaAs interface.[27] In conclusion, defects at the interface—possibly missing Ga atoms—are responsible for the weak temperature dependence of the barrier height and its low absolute value for the group 2 contacts.

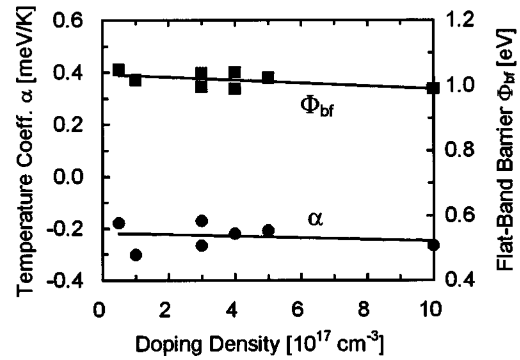

FIG. 4. Flatband barrier height and temperature coefficient of the Schottky diodes of group 1 as a function of doping density. Both parameters decrease weakly with increasing doping density.

A plot of both, the flatband barrier height and the temperature coefficient for the diodes of group 1, as a function of the doping density is shown in Fig. 4. The dependence of the barrier height on the doping density is small. A linear fit to the data yields a dependence of $-4.4\ \text{meV}/(10^{17}$ donors). The same situation holds for the temperature coefficient which decreases with the doping density by $-3.0\ \text{meV}/(K\times10^{17}$ donors). A possible explanation is the well known fact that the gap energy decreases with increasing doping.[28] Therefore one also expects a decrease of the barrier height. However the data are not accurate enough to make any quantitative statement.

V. SUMMARY

In this study two groups of Pt/n-GaAs Schottky contacts could be identified. They differ in the barrier height itself as well as in the temperature dependence of the barrier height. Group 1 contacts have a barrier height of about 1 eV which increases with decreasing temperature while group 2 contacts have a lower barrier height of about 0.9 eV which is almost independent of the temperature. Barrier height and temperature dependence of the group 1 contacts are determined by the direct and the indirect energy gap as proposed by the model of Tersoff. The negligible temperature dependence as well as the lower barrier of the group 2 contacts suggest that interface defects are responsible for the pinning of the Fermi level because their ionization entropy is only weakly dependent on the temperature. The tendency that high barriers show a stronger temperature dependence than low barriers was also observed by Werner and Güttler for different materials on Silicon.[22] However, no explanation was given. The fact that even diodes which are from the same batch belong to the two different groups indicates that great care has to be taken during the technological processes. Even a small number of defects can deteriorate the quality of the metal–semiconductor interface and strongly affect the electrical characteristics of the Schottky diodes.

ACKNOWLEDGMENTS

The authors would like to thank T. W. Crowe and J. L. Hesler for providing the computer program which was used for data acquisition.

[1] H. P. Röser, Infrared Phys. **32**, 385 (1991).
[2] R. Titz, M. Birk, D. Hausamann, R. Nitsche, F. Schreier, H. Küllmann, and H. P. Röser, Infrared Phys. Technol. **36**, 883 (1995).
[3] U. O. Frisk, ESA SP **401**, 365 (1997).
[4] G. J. Melnick *et al.*, ESA SP **401**, 189 (1997).
[5] J. W. Bowen *et al.*, ESA SP **388**, 183 (1996).
[6] H.-W. Hübers, G. W. Schwaab, and H. P. Röser, J. Appl. Phys. **75**, 4243 (1994).
[7] H. P. Röser, G. W. Schwaab, R. U. Titz, and M. F. Kimmitt, J. Appl. Phys. **72**, 3194 (1992).
[8] H. P. Röser, H.-W. Hübers, E. Bründermann, and M. F. Kimmitt, Semicond. Sci. Technol. **11**, 1328 (1996).
[9] J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984).
[10] J. Tersoff, Phys. Rev. B **32**, 6968 (1985).
[11] P. Revva, J. M. Langer, M. Missous, and A. R. Parker, J. Appl. Phys. **74**, 416 (1993).
[12] A. Aydinli and R. J. Mattauch, Solid-State Electron. **25**, 551 (1982).
[13] T. Suzuki, H. Shinohara, K. Mizuno, H. P. Röser, and R. Titz, Proceedings of the Third Asia-Pacific Microwave Conference, Tokyo, 1990, p. 1081.
[14] T. Hashizume, H. Hasegawa, T. Sawada, A. Grüb, and H. L. Hartnagel, Jpn. J. Appl. Phys., Part 1 **32**, 486 (1993).
[15] W. Mönch, *Semiconductor Surfaces and Interfaces*, 2nd ed. (Springer, Berlin, 1995).
[16] Farran Technology Ltd, Cork, Ireland, 1988.
[17] V. Krozer and A. Grüb, Solid-State Electron. **37**, 169 (1994).
[18] W. C. B. Peatman and T. W. Crowe, Int. J. of Infrared Millim. Waves **11**, 355 (1990).
[19] W. C. B. Peatman, P. A. D. Wood, D. Porterfield, T. W. Crowe, and M. J. Brooks, Appl. Phys. Lett. **61**, 294 (1992).
[20] L. F. Wagner, R. W. Young, and A. Sugarman, IEEE Electron Device Lett. **EDL-4**, 320 (1983).
[21] V. W. L. Chin, M. A. Green, and J. W. V. Storey, J. Appl. Phys. **68**, 3470 (1990).
[22] J. H. Werner and H. H. Güttler, J. Appl. Phys. **73**, 1315 (1993).
[23] E. Y. Chan, H. C. Card, E. S. Yang, A. R. Kerr, and R. J. Mattauch, IEEE Trans. Electron Devices **ED-26**, 214 (1979).
[24] J. S. Blakemore, J. Appl. Phys. **53**, R123 (1982).
[25] P. S. Ho, M. Liehr, P. E. Schmid, F. K. Legoues, E. S. Yang, H. L. Evans, and X. Wu, Surf. Sci. **168**, 184 (1986).
[26] W. E. Spicer, I. Lindau, P. Skeath, C. Y. Su, and P. Chye, Phys. Rev. Lett. **44**, 420 (1980).
[27] C. Fontaine, T. Okumura, and K. N. Tu, J. Appl. Phys. **54**, 1404 (1983).
[28] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981).