Thermal reaction of Pt film with ⟨110⟩ GaN epilayer

S. M. Gasser,[a] E. Kolawa, and M.-A. Nicolet
California Institute of Technology, Pasadena, California 91125

(Received 26 February 1999; accepted 25 June 1999)

Backscattering spectrometry, x-ray diffractometry, and scanning electron microscopy have been used to study the reaction of a thin Pt film with an epilayer of ⟨110⟩ GaN on ⟨110⟩ sapphire upon annealing at 450, 550, 650, 750, and 800 °C for 30 min. A Ga concentration of 2 at. % is detected by MeV $^4He^{++}$ backscattering spectrometry in the Pt layer at 550 °C. By x-ray diffraction, structural changes are observed already at 450 °C. At 650 °C, textured Ga_2Pt appears as reaction product. The surface morphology exhibits instabilities by the formation of blisters at 650 °C and voids at 800 °C. © *1999 American Vacuum Society.* [S0734-2101(99)10705-X]

I. INTRODUCTION

In the past few years, GaN has become of great interest for applications in blue and ultraviolet lasers, light emitting diodes, photodetectors, and high-temperature/high-power electronic devices.[1,2] Such applications entail superior requirements for the metal contacts used in the electrical circuits. High current densities are usually involved in laser applications. A demand for low-resistance ohmic contacts therefore arises. For high-power devices, rectifying contacts with a high Schottky barrier height and breakdown voltage are essential. The operating conditions of these applications often involve elevated temperatures. Thermal stability is, therefore, a prerequisite. For compound semiconductor metallizations, the knowledge of ternary or even quaternary phase diagrams is highly desirable. Those are complicated and not very well known. The pursuit of finding contacts that satisfy entirely is a challenge. On the other hand, the choice of a metal as contact for *n*-type as well as for *p*-type GaN is facilitated because indications exist that the barrier height depends on the metal work function.[3–10] The lack of Fermi level pinning at the metal/semiconductor interface is predicted by the ionic nature of GaN.[11] However, the dependence of the barrier height on the metal work function does not follow a linear relation of unity slope as predicted by the Schottky model,[12] and interfacial reactions between the metal and the GaN substrate further affect this relationship.[13]

Schottky contacts on *n*-type GaN have not received much attention yet. Au (as-deposited),[3,14] Pt and Pd,[1,15–17] Ni,[13,18] and PtSi[19] were reported to have rectifying characteristics. Platinum with its high work function of 5.65 eV[20] exhibits ideal Schottky behavior on *n*-type GaN with a high barrier height.[15,21] A GaN metal–semiconductor field effect transistor (MESFET) with Au/Pt as Schottky gate is reported to withstand heating in nitrogen at 400 °C for 1000 h.[22] Other authors, though, report the degradation of Pt diodes after annealing at 400 °C for 1 h.[19] Low-resistance, ohmic contacts to *p*-type GaN are achieved by using metals with a high work function,[8] and indeed, Pt or Pd yield a lower value of the total resistance compared to other metals.[7–10]

Platinum is not stable with GaN.[23] The reaction at the interface between a Pt film and a GaN substrate is poorly investigated.[24] Metallurgical investigations are required to understand the reaction process at the metal-GaN interface upon thermal stressing. Platinum metal contacts are investigated here before and after vacuum annealing at temperatures between 450 and 800 °C for 30 min in a conventional evacuated tube furnace. The films are analyzed by 2.0 MeV $^4He^{++}$ backscattering spectrometry for elemental depth profiling, x-ray diffraction for phase identification, and by scanning electron microscopy to visualize the surface morphology.

II. EXPERIMENT

Pieces of an autodoped ($n = 4 \times 10^{16}$ cm^{-3}) 1.8-μm-thick *n*-type epitaxial layer of ⟨110⟩ GaN grown by metalorganic chemical vapor deposition (MOCVD) on a ⟨110⟩ sapphire substrate was used for this study. Prior to insertion into the deposition system, the substrates were ultrasonically degreased subsequently in trichloroethylene, acetone, and methanol, and chemically etched with NH_4OH diluted ten times in deionized water. This etch is a good premetallization surface treatment for GaN *n*-type ohmic contacts.[25]

70-nm-thick Pt films were deposited on GaN by rf-magnetron sputtering with argon in a cryopumped vacuum system of 5×10^{-7} Torr base pressure. The samples were then annealed in a quartz vacuum-tube furnace (base pressure 5×10^{-7} Torr) at various temperatures between 450 and 800 °C for 30 min. Each sample was annealed just once.

Elemental depth profiles were measured by 2.0 MeV $^4He^{++}$ backscattering spectrometry with a scattering angle of 167° for the detected particles. An Inel position-sensitive multichannel detector was used to obtain structural information by Debye–Scherrer x-ray diffraction with a collimated Co $K\alpha$ beam incident on the sample at a glancing angle of 12°. The Bragg angle was calibrated using Si powder as a standard. Selected samples were analyzed by Read camera x-ray diffraction with a collimated Cu $K\alpha$ beam. Scanning electron micrographs were taken on a Cambridge Stereoscan 250 Mk2 with a Kevex energy dispersive spectrometer. The 10 keV beam spot for energy dispersive x-ray mapping had a diameter of 83 nm.

[a]Electronic mail: sgasser@cco.caltech.edu

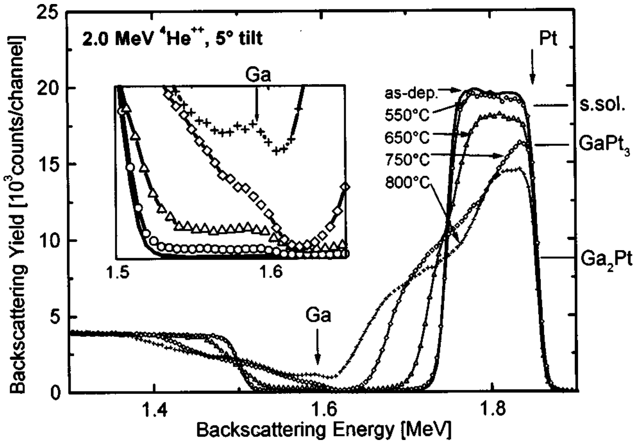

FIG. 1. 2.0 MeV $^4He^{++}$ backscattering spectra of ⟨GaN⟩/Pt samples before and after annealing at 550, 650, 750, and 800 °C for 30 min. Inserted are the spectra magnified in the energy range between 1.5 and 1.65 MeV; near the surface energy position of Ga (1.59 MeV).

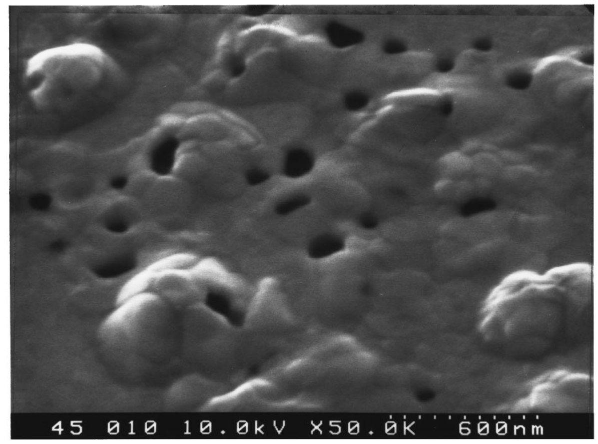

FIG. 2. Scanning electron micrograph of ⟨GaN⟩/Pt annealed at 650 °C for 30 min.

III. RESULTS

The evolution upon thermal stressing of the atomic depth distribution between the Pt thin film and the GaN substrate is shown in Fig. 1. The spectrum of the as-deposited sample displays a uniform layer with a sharp interface at the substrate. No changes were observed in the backscattering spectrum after annealing at 450 °C (not shown). At 550 °C, the Pt signal is slightly lowered and a uniform and flat plateau-like Ga signal appears between its substrate and surface energy positions. To clearly depict this plateau-like signal, the spectra in the energy range between 1.5 and 1.65 MeV near the surface energy position of Ga (1.59 MeV) are magnified in the insert of the figure.

Two possibilities exist to explain the extension of the Ga signal to its surface energy position. Either Ga is distributed uniformly in the Pt layer, or holes have been formed in the layer upon annealing so that the beam can hit the GaN substrate surface directly in small areas. According to the binary phase diagram, Ga can enter into solid solution with Pt up to 6 at. % of Ga at room temperature, and 14 at. % at 1361 °C.[26] The spectrum of the sample annealed at 550 °C corresponds to about 2 at. % Ga distributed uniformly in the Pt film and is quantitatively consistent with the slight reduction of the Pt signal. Holes in the Pt film would leave the height of the Pt signal unchanged. A significant dissolution of Ga in Ni was also observed as the first step in the reaction of a Ni film with GaN.[18,27] The similarity between Ni and Pt is mentioned further in the following section.

At 650 °C, the reduction of the Pt backscattering signal corresponds to a value of about 13 at. % of Ga, which clearly exceeds the limit of solid solubility of ~7.3 at. % at that temperature. Therefore, either a reaction must have taken place, or a nonuniform distribution of the film has developed. Indeed, some blisters are observed by either scanning electron or optical microscopy already at 550 °C, but their number is few. The blisters are distributed nonuniformly and appear to break up and lead to the formation of holes in the Pt layer. Figure 2 shows a scanning electron micrograph of the sample annealed at 650 °C, taken from a surface area with a high density of blisters.

The broadening of the Pt and Ga backscattering signals at the interface at 650 °C indicates interaction between the GaN substrate and the Pt metallization. Annealing at 750 and 800 °C leads to further broadening and lowering of the Pt signal. Vertical marks in Fig. 1 position the yield of the Pt signal for uniform layers of the three possible reaction products: a saturated Pt(Ga) (6 at. % Ga, at room temperature), $GaPt_3$, or Ga_2Pt, in all cases neglecting possible incorporations of nitrogen. The evolution of the Ga signal with rising annealing temperatures indicates an extension of the interaction between the Pt and GaN into deeper levels of the substrate.

A scanning electron micrograph of a sample surface after annealing at 800 °C is shown in Fig. 3. Voids are observed on the whole surface, and they are bigger than the holes that appeared at 650 °C (see Fig. 2, notice the different scales). Energy dispersive spectroscopy of induced x-rays inside and outside of the voids give Ga:Pt ratios of 1.13 and 1.17, respectively, that differ insignificantly from each other. Plati-

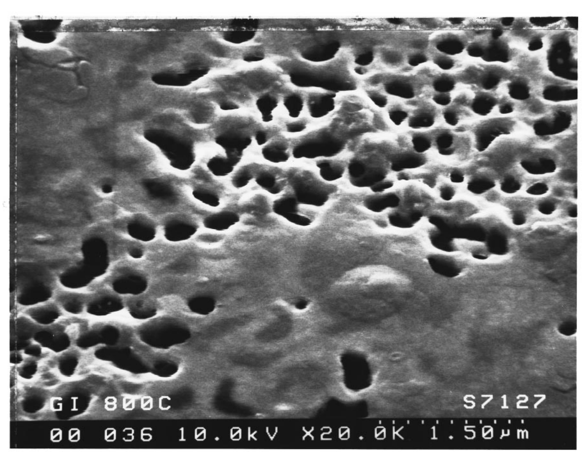

FIG. 3. Scanning electron micrograph of ⟨GaN⟩/Pt annealed at 800 °C for 30 min.

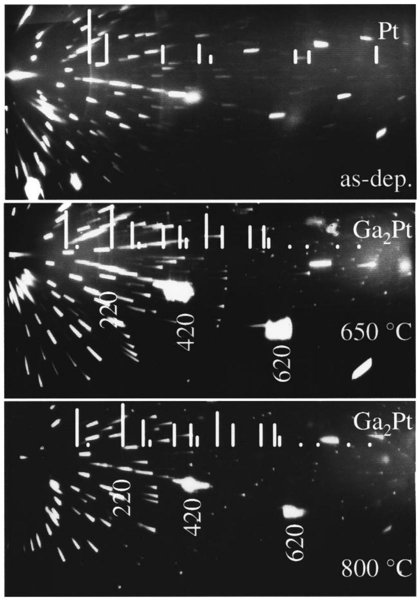

FIG. 4. Read camera x-ray diffraction pattern of ⟨GaN⟩/Pt, as-deposited (top) and after annealing at 650 °C (middle) and 800 °C (bottom). Positions and intensities of Pt and Ga_2Pt powder diffraction peaks are inserted with white lines.

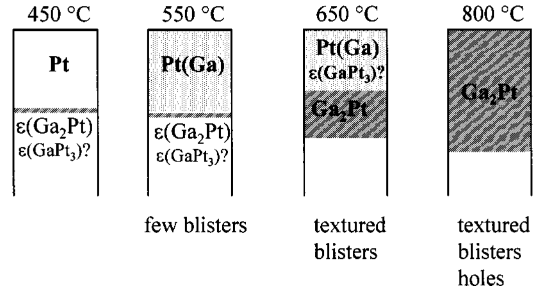

FIG. 5. Sequence of reaction of Pt thin films on ⟨GaN⟩ substrate upon annealing in vacuum; sketch derived from backscattering and x-ray diffraction spectra.

num must therefore still be present on the bottom of the holes. Backscattering spectra of laterally uneven samples as revealed by Figs. 2 and 3 are difficult to interpret because they become ambivalent.

Attempts to obtain crystallographic information of annealed films by interpreting Inel x-ray diffraction spectra were also ambiguous, suggesting either a near-amorphous structure or a highly textured reacted layer. To search for texture, two-dimensional x-ray diffraction photographs were taken using a Read camera and are shown in Fig. 4. The Read camera x-ray diffraction pattern of the as-deposited sample (Fig. 4, top) shows diffraction lines originating from pure platinum. The sample annealed at 450 °C shows additional diffraction lines that can be assigned to the (220) and (420) reflections of the Ga_2Pt phase. Their intensities are according to the powder diffraction data file,[28] indicating randomly oriented Ga_2Pt grains at 450 °C. The x-ray diffraction photograph of the sample annealed at 650 °C (Fig. 4, middle) displays uniformly distributed Pt reflections as well as reflections that are concentrated in wide diffraction spots. These can be assigned to the Ga_2Pt (420) and (620) reflections and indicate texture. The diffraction picture of the sample annealed at 800 °C (Fig. 4, bottom) still exhibits the Ga_2Pt diffraction spots that were visible at 650 °C, but less pronounced, together with weak continuous diffraction lines, also from Ga_2Pt. Platinum lines have disappeared at 800 °C. For comparison, the positions and intensities of Pt (top) and Ga_2Pt (middle and bottom) powder diffractions are inserted in Fig. 4 with white lines.

Figure 5 sketches a geometrically idealized sequence of reaction as it can be surmised from the backscattering and x-ray diffraction spectra. Apart from the appearance of x-ray diffraction lines of Ga_2Pt already at 450 °C, blister formation is clearly correlated with the reaction between Pt and Ga to Ga_2Pt. A possible existence of $GaPt_3$ as an intermediate reaction phase is discussed below.

IV. DISCUSSION

Although no indications of a change is noticeable between the backscattering spectra of the as-deposited sample and that annealed at 450 °C, the Read camera x-ray diffraction picture of the latter clearly shows patterns that cannot be attributed anymore to pure Pt. Similarly, Liu *et al.* observed a degradation of Pt diodes without visible changes in the backscattering spectrum after annealing at 400 °C for 1 h in a N_2 flow.[19] These authors further report the appearance of bubbles on the Pt surface after 2 h. Duxstad *et al.* report on small particles of Pt on the surface of the Pt film after thermal treatment in flowing N_2 at 600 °C for 30 min.[17] We observe the formation of blisters after vacuum annealing at 550 °C for 30 min, and more so at 650 °C (see also Fig. 2). Their presence is correlated with the growth of Ga_2Pt. Hence, it could be that the blisters and holes are caused by the build-up of gas pressure from released nitrogen at the interface to the substrate. The dissociation of bare GaN sets in at about 800 °C,[29] but a reaction with Pt could greatly enhance the diffusion of nitrogen. In molecular beam epitaxy, the temperature range around 800 °C is a boundary between liquid Ga droplet formation and single crystal growth of GaN.[30]

Thermodynamic considerations of the Pt–Ga–N system at 600 °C by Mohney *et al.* predict Pt to react with GaN to form Pt gallides and release N_2 gas.[23] We indeed observe the formation of Pt gallides. Which gallide of Pt should form depends on the nitrogen partial pressure.[23] To the best of our knowledge, no clear experimental evidence of such a dependency on the nitrogen gas pressure is published. Moreover, our anneals were performed in vacuum which corresponds to an open system where thermodynamics are strictly not applicable. How stable the Ga_2Pt phase in contact with GaN is can thus not be elucidated from the phase diagram.

Nickel resembles Pt chemically and neither forms nitrides under normal conditions. The thermodynamic predictions are the same for Ni as for Pt.[23] The release of N_2 gas has clearly been observed in the GaN–Ni system that has been investigated more thoroughly than Pt.[13,18] Bermudez *et al.* report a large N_2 pressure burst at 600 °C in ultrahigh vacuum.[27] Venugopolan *et al.* observed the release of N_2 gas from the ⟨GaN⟩/Ni reaction at 750 °C in either Ar or N_2, even when the nitrogen pressure was 1 atm,[18] as opposed to 600 °C in vacuum.[27] In the present study, the loss of nitrogen is indicated by blister formation already at 550 °C. The difference of temperatures may be related to the fact that by Miedema's model calculations of heats of formation of gallides, Pt has a higher chemical affinity to GaN than Ni.[31]

Island formation upon annealing of thin metal films on GaN is reported in the literature with Ni above 800 °C,[32] Pt above 725 °C, and Pd above 700 °C, and is explained with the difference of surface energies between thin metal films and ceramics that causes dewetting.[17] Moreover, differences in the thermal expansion coefficients can generate compressive stress in the metal film and deformation of the film, as observed in our study, or delamination, as it is noted with Pd.[17] The linear coefficients of thermal expansion of materials involved here are (in units of $\times 10^6$/°C): Pt:9; Ga:18; $\langle Al_2O_3 \rangle$:5–7;[33] GaN:5.6.[34] We interpret the observed formation of blisters with holes as the result of nitrogen effusion from the underlying substrate. These blisters also offer a means to release compressive stress.

Work that was performed with Pt thin films on GaAs shows that the first phase that forms is GaPt, after annealing in argon, air, or vacuum.[35] Previous to the crystallization of $GaPt_3$, which is epitaxially matched to the Pt phase, a solid-state amorphization reaction is observed.[36] $GaPt_3$ has a diffraction pattern almost identical to that of Pt except for a few very weak lines,[35] and it is the first binary compound in the phase diagram that equilibrates with the Pt–Ga solid solution by addition of Ga. Hence, it is quite possible that some $GaPt_3$ forms initially in our samples too, but that it remains undetected by x-ray diffraction, before Ga_2Pt starts to form. The backscattering spectrum excludes the presence of significant amounts of $GaPt_3$ up to 550 °C. At 650 °C, however, substantial amounts of that phase could also be assumed to exist next to Ga_2Pt while still preserving consistency with both the backscattering spectrum in Fig. 1 and the x-ray data.

V. SUMMARY AND CONCLUSIONS

The solid-state reaction between Pt thin films and GaN substrate starts around 550 °C. Crystallization of highly textured Ga_2Pt is observed at 650 °C. Morphological instabilities with blister and void formation appear at 650 °C and above. An open question is the strong, theoretically predicted dependency of the equilibrium state on the nitrogen partial pressure in the ternary Ga–Pt–N system. The applied method of vacuum annealing in this investigation does not correspond to a closed system setup. It is known that diffusion barriers can, besides other benefits, provide efficient encapsulation and retard the deterioration of volatile semiconductors such as GaAs[37–40] or InP.[41] Hence, it would be of great interest to further study the ⟨GaN⟩/Pt metal contact in a practically closed system realized by capping it with a diffusion barrier.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Center for Integrated Space Microsystems at JPL/NASA. Their gratitude also goes to Dr. Alex Dommann, Neu-Technikum Buchs, Switzerland, who supplied the GaN substrate, and helped them completing and interpreting the Read camera measurements. They also thank Rob Gorris and Mike Easterbrook for their technical assistance.

[1] S. N. Mohammad and H. Morkoç, Prog. Quantum Electron. **20**, 361 (1996).
[2] H. Morkoç, S. Strite, G. B. Gao, M. E. Lin, B. Sverdiov, and M. Burns, J. Appl. Phys. **76**, 1363 (1994).
[3] J. S. Foresi and T. D. Moustakas, Appl. Phys. Lett. **62**, 2859 (1993).
[4] S. C. Binari, H. B. Dietrich, G. Kelner, L. B. Rowland, K. Doverspike, and D. K. Gaskill, Electron. Lett. **30**, 909 (1994).
[5] T. U. Kampen and W. Mönch, Appl. Surf. Sci. **117**, 388 (1997).
[6] Q. Z. Liu and S. S. Lau, Solid-State Electron. **42**, 677 (1998).
[7] H. Ishikawa, S. Kobayashi, Y. Koide, S. Yamasaki, S. Nagai, J. Umezaki, M. Koike, and M. Murakami, J. Appl. Phys. **81**, 1315 (1997).
[8] Y. Koide, H. Ishikawa, S. Kobayashi, S. Yamasaki, S. Nagai, J. Umezaki, M. Koike, and M. Murakami, Appl. Surf. Sci. **117**, 373 (1997).
[9] J. K. Kim, J.-L. Lee, J. W. Lee, H. E. Shin, Y. J. Park, and T. Kim, Appl. Phys. Lett. **73**, 2953 (1998).
[10] J. S. Jang, I. S. Chang, H. K. Kim, T. Y. Seong, S. H. Lee, and S. J. Park, Appl. Phys. Lett. **74**, 70 (1999).
[11] S. Kurtin, T. C. McGill, and C. A. Mead, Phys. Rev. Lett. **22**, 1433 (1969).
[12] A. C. Schmitz, A. T. Ping, M. A. Khan, Q. Chen, J. W. Yang, and I. Adesida, J. Electron. Mater. **27**, 255 (1998).
[13] J. D. Guo, F. M. Pan, M. S. Feng, R. J. Guo, P. F. Chou, and C. Y. Chang, J. Appl. Phys. **80**, 1623 (1996).
[14] P. Hacke, T. Detchprohm, K. Hiramatsu, and N. Sawaki, Appl. Phys. Lett. **63**, 2676 (1993).
[15] J. D. Guo, M. S. Feng, R. J. Guo, F. M. Pan, and C. Y. Chang, Appl. Phys. Lett. **67**, 2657 (1995).
[16] L. Wang, M. I. Nathan, T.-H. Lim, M. A. Khan, and Q. Chen, Appl. Phys. Lett. **68**, 1267 (1996).
[17] K. J. Duxstad, E. E. Haller, and K. M. Yu, J. Appl. Phys. **81**, 3134 (1997).
[18] H. S. Venugopalan, S. E. Mohney, B. P. Luther, S. D. Wolter, and J. M. Redwing, J. Appl. Phys. **82**, 650 (1997).
[19] Q. Z. Liu, L. S. Yu, S. S. Lau, J. M. Redwing, N. R. Perkins, and T. F. Kuech, Appl. Phys. Lett. **70**, 1275 (1997).
[20] *CRC Handbook of Chemistry and Physics* (CRC, Cleveland, OH, 1994/1995).
[21] S. N. Mohammad, Z. Fan, A. E. Botcharev, W. Kim, O. Aktas, A. Salvador, and H. Morkoç, Electron. Lett. **32**, 599 (1996).
[22] S. Yoshida and J. Suzuki, J. Appl. Phys. **84**, 2940 (1998).
[23] S. E. Mohney and X. Lin, J. Electron. Mater. **25**, 811 (1996).
[24] C. I. Wu and A. Kahn, J. Vac. Sci. Technol. B **16**, 2218 (1998).
[25] L. F. Lester, J. M. Brown, J. C. Ramer, L. Zhang, S. D. Hersee, and J. C. Zolper, Appl. Phys. Lett. **69**, 2737 (1996).
[26] T. B. Massalski, *Binary Alloy Phase Diagrams*, 2nd ed. (ASM International, Metals Park, OH, 1990).
[27] V. M. Bermudez, R. Kaplan, M. A. Khan, and J. N. Kuznia, Phys. Rev. B **48**, 2436 (1993).
[28] 1995 JCPDS-International Center for Diffraction Data, PDF-2, File No. 03-1007.
[29] R. Groh, G. Gerey, L. Bartha, and J. I. Pankove, Phys. Status Solidi A **26**, 353 (1974).
[30] M. V. Averyanova, S. Y. Karpov, Y. N. Makarov, I. N. Przhevalskii, M. S. Ramm, and R. A. Talalaev, MRS Internet J. Nitride Semicond. Res. **1**, 31 (1996).
[31] F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema, and A. K. Niessen, in *Cohesion and Structure Vol. 1*, edited by F. R. de Boer and D. G. Pettifor (North–Holland, Amsterdam, 1988).
[32] H. S. Venugopalan, S. E. Mohney, J. M. DeLucca, B. P. Luther, and G. E. Bulman, J. Vac. Sci. Technol. A **16**, 607 (1998).

[33] *CRC Handbook of Tables for Applied Engineering Science*, edited by R. E. Bolz and G. L. Tuve (CRC, Cleveland, OH, 1970).
[34] H. Hartnagel, Mater. Sci. Eng., B **29**, 47 (1995).
[35] V. Kumar, J. Phys. Chem. Solids **36**, 535 (1975).
[36] D. H. Ko and R. Sinclair, J. Appl. Phys. **72**, 2036 (1992).
[37] A. Tamura, Y. Ikeda, T. Yokoyama, and K. Inoue, J. Appl. Phys. **67**, 6171 (1990).
[38] J. M. Molarius, E. Kolawa, K. Morishita, J. L. Tandon, and M.-A. Nicolet, J. Electrochem. Soc. **138**, 834 (1991).
[39] U. Merkel, E. Nebauer, and M. Mai, Thin Solid Films **217**, 2424 (1992).
[40] J. S. Chen, E. Kolawa, R. P. Ruiz, and M.-A. Nicolet, J. Appl. Phys. **75**, 7373 (1994).
[41] J. S. Reid, R. P. Ruiz, E. Kolawa, J. S. Chen, J. Madok, and M.-A. Nicolet, Mater. Res. Soc. Symp. Proc. **260**, 555 (1992).