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Growth-mode modification of Bi on CdTe(111)*A* using Te monolayer deposition

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Bi deposited on the CdTe(111)*A* (Cd-terminated) surface grows by three-dimensional (3D) islanding, while Bi deposited on the CdTe(111)*B* (Te-terminated) grows layer-by-layer. However, introducing a Te monolayer (ML) on the CdTe(111)*A* surface reduces the interfacial energy, thereby changing the growth mode of Bi from 3D islandlike to layer-by-layer growth. The Te ML remains where it is deposited, which differs from the growth mode in which the surface-active agent floats on the growing surface. By incorporating appropriate Te ML's, Bi/CdTe superlattices with sharper interfaces were observed. These superlattices were characterized by x-ray diffraction and transmission electron microscopy. [S0163-1829(98)01027-3]

I. INTRODUCTION

Three different growth modes are generally classified in heteroepitaxy: layer-by-layer (Frank–Van der Merwe) growth, three-dimensional (3D) island (Volmer-Weber) growth, and layer-by-layer growth followed by island (Stranski-Krastanov or SK) growth. The observed growth mode depends upon the surface free energy, the lattice mismatch (misfit), and the crystal structures of the growing film and substrate. For the lattice-matched case, layer-by-layer growth occurs when $\gamma_f+\gamma_i<\gamma_s$, where γ_f, γ_i, and γ_s are the surface free energies of the film surface, the substrate-film interface, and the substrate surface, respectively. On the other hand, when $\gamma_f+\gamma_i>\gamma_s$, 3D island growth will occur in order to minimize the interface areas. The SK growth mode generally occurs when $\gamma_f+\gamma_i\approx\gamma_s$ in lattice-mismatched systems.

3D nucleation is regarded as undesirable because it may introduce height variations and a number of defects where the 3D islands coalesce. This is particularly undesirable for various planar devices such as quantum wells and superlattices (SL's), which require uniform thickness and low defect densities as well as sharp interfaces. In a SL geometry of two elements *A* and *B*, one combination of them (*A*/*B* or *B*/*A*) will not satisfy the Young inequality. Consequently, if *A* grows on *B* in a layer-by-layer mode, then *B* grows on *A* in either a 3D island or an SK mode, which is an obstacle for SL growth. This behavior has been observed in the growth of Bi and CdTe SL's.[1] Therefore, in the growth of a SL with sharp interfaces we need to change the growth mode from 3D island or SK to layer-by-layer growth. There has been considerable interest in developing methods for controlling nucleation characteristics. Reducing the temperature or increasing the growth rate suppresses 3D island nucleation during SK growth.[2] Very-low-energy, high flux Ar-ion irradiation during molecular-beam epitaxy has been shown to suppress the SK growth of GaAs on Si(100), approaching a layer-by-layer growth.[3] Introducing a foreign surface species such as As as a surfactant has been shown to enhance layer-by-layer growth of Ge on Si.[4] A number of materials have been investigated as surfactants[4–33] (e.g., H, Ga, In, Sn, Pb, Bi, Sb, As, and Te) in a wide variety of material systems; the surfactant plays a role in wetting the surface, thereby enhancing the layer-by-layer growth. In the presence of a surfactant the surface tensions γ_f, γ_i, and γ_s would be altered to new values, which we write as γ_f', γ_i', and γ_s'. The wetting inequality, given above, would now take the form $\gamma_f'+\gamma_i'\leqslant\gamma_s'$. If a surfactant permits the film being deposited to wet an otherwise unwettable surface, the concentrations of the surfactant on the free surface and the interface must be determined independently. According to the literature, most surfactants tend to float to the free surface. On the other hand, there have been contradictory reports concerning Te-mediated growth-mode modification,[28–33] as will be discussed further below.

In this paper, we report that on the CdTe(111)*A* surface a Te ML modifies the growth mode of a Bi layer from 3D islandlike to layer-by-layer and does not segregate on the growth front. When the method was applied to the Bi/CdTe SL system, smooth, sharp interfaces were observed. This result may allow the use of Bi-based SL's in the area of quantum transport and in devices such as thermoelectric coolers.[34,35]

II. Te SURFACTANT EFFECTS ON Bi THIN-FILM GROWTH

Our Bi thin films and Bi/CdTe SL's were grown on semi-insulating CdTe(111)*A*/*B* substrates in a custom-built MBE system similar in design to a Varian model 360. The system is equipped with RHEED and AES, and the base pressure of the growth chamber is in the 10^{-10} Torr range. CdTe(111) substrates were chosen due to the small (0.7%) lattice mismatch with (00.1) Bi. The substrates were etched in a solu-

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tion of 1% bromine in methanol prior to placing them in the load-lock chamber. Before the Bi was deposited, a 3000 Å CdTe buffer layer was grown on the CdTe(111) substrate at 250 °C. The growth direction of the Bi layer on CdTe(111) is parallel to the trigonal axis of Bi. RHEED was used to examine the specific surface reconstruction of the deposited layers. The growth temperature of the Bi thin films and Bi/CdTe SL's was 100 °C, and a typical growth rate was 0.4 Å/s.

In the zinc-blende structure, the two (111) faces, designated by *A* and *B*, are different from one another and polar. In CdTe, the *A* face is terminated by triply bonded Cd atoms, while triply bonded Te atoms terminate the *B* face. It is well known[36] that the *A* face may have different surface reconstruction than the *B* face and that these differences may be examined by RHEED. The CdTe(111)*B* face has a $(2\sqrt{3} \times 2\sqrt{3}\text{-}R30°)$ reconstruction, which results in the RHEED pattern displaying 1/2 integer order streaks in the (110) azimuth and 1/6 integer order in the (112) azimuth. On the other hand, the CdTe(111)*A* face has a (2×2) reconstruction resulting in a RHEED pattern with 1/2 integer orders in both the (112) and (110) azimuths.

It has been reported[1] that Bi deposited on the CdTe(111)*A* (Cd-terminated) surface displays 3D island growth, while Bi deposited on the CdTe(111)*B* (Te-terminated) surface grows layer-by-layer. Figures 1(a) and 1(e) show the RHEED patterns of 3000 Å CdTe buffer layers from the (111)*B* and (111)*A* surfaces, respectively, for the (110) azimuth. For Te-terminated (111)*B*, the RHEED patterns during subsequent Bi deposition showed no reconstruction. The diffraction streaks were sharp and Kikuchi lines were evident, as shown in Figs. 1(b), 1(c), and 1(d). This *in situ* evidence confirms a uniform 2D layer-by-layer growth of the Bi layers on CdTe(111)*B*. However, Bi layers grown on Cd-terminated (111)*A* exhibited a spotty RHEED pattern during the first ~50 Å growth [Figs. 1(f) and 1(g)]. As the deposition continued, the spotty pattern gave way to a streaked pattern [Fig. 1(h)]. This difference in growth mode between (111)*A* and (111)*B* arises because the Cd-terminated and Te-terminated surfaces are physically different. It suggests that modification of the Bi growth mode on CdTe(111)*A* might be achieved by depositing a Te ML, thereby replacing the previously Cd-terminated faces with Te. The arriving Bi species would then see a Te-terminated face and grow layer-by-layer, as on the *B* face. A growth mode modification of Bi on CdTe(111)*A* is required if one is to fabricate high-quality Bi/CdTe SL's, as will be discussed later.

The RHEED patterns along the $(1\bar{1}0)$ azimuth for the initial stages of Bi growth on CdTe(111)*A* with a Te ML are shown in Fig. 2. Now the RHEED pattern shows a (4×2) surface reconstruction, as shown in Figs. 2(a) and 2(b). And instead of the spotted patterns which occur on the CdTe(111)*A* face, the Bi growth on newly Te-terminated CdTe(111)*A* layers shows a streaky pattern, providing evidence of layer-by-layer growth. These results imply that the Te ML serves to reduce the interface free energy in the Bi/CdTe(111)*A* system. In an XPS study, we could not find Te on the free surface of a 150 Å Bi layer grown on Te-terminated CdTe(111)*A*, and only a small amount of Te (about 0.08%) was detected in the bulk of the film after a 30 Å surface layer was removed. These measurements could not provide any reliable information concerning whether a Te layer is present at the Bi/CdTe interface, due to the large contribution of the CdTe substrate to the XPS signal. In spite of this limitation, however, the XPS study suggests that the Te does not float on the growth front. This conclusion is also supported by a RHEED experiment. The initial growth stages [e.g., the first 2 Å of Bi growth on a Te-terminated CdTe(111)*A* surface as in Figs. 2(c) and 2(d)], were found to yield an unreconstructed Bi pattern rather than a Te ML pattern, implying that the Te ML does not segregate to the Bi surface. From XPS and RHEED studies, we therefore conclude that Te remains at the Bi/CdTe(111)*A* interface, possibly forming Cd-Te bonds, and that the excess Te may be incorporated into the growing films. Thus a Te ML on polar CdTe(111)*A* works as a beneficial surface-active agent, which reduces the surface free energy of the substrate and bonds to the substrate, forming a Te layer. Rodrigues *et al.*[32] reported that about 0.5 ML of Te suppressed the island growth of InAs on GaAs for up to 17 ML, and remained at the InAs/GaAs interface as determined with XPS and Rutherford backscattering spectroscopy (RBS). Ohtake *et al.*[33] observed that ZnSe grows on GaAs in a layer-by-layer mode

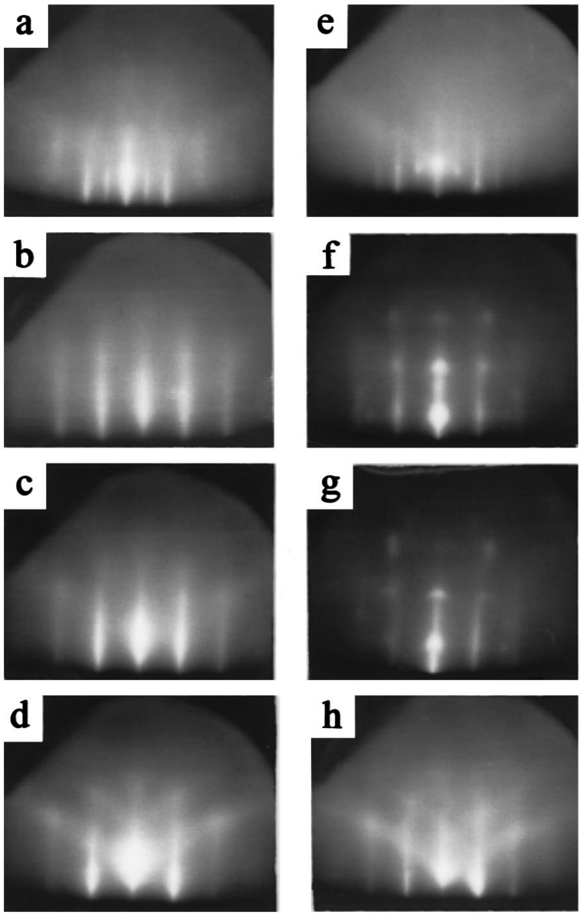

FIG. 1. RHEED patterns of deposited layers: (a) CdTe(111)*B* buffer layer–(110) azimuth, (b) 5 Å Bi grown on CdTe(111)*B*, (c) 10 Å Bi grown on CdTe(111)*B*, (d) 100 Å Bi grown on CdTe(111)*B*, (e) CdTe(111)*A* buffer layer–(110) azimuth, (f) 5 Å Bi grown on CdTe(111)*A*, (g) 30 Å Bi grown on CdTe(111)*A*, and (h) 100 Å Bi grown on CdTe(111)*A*.

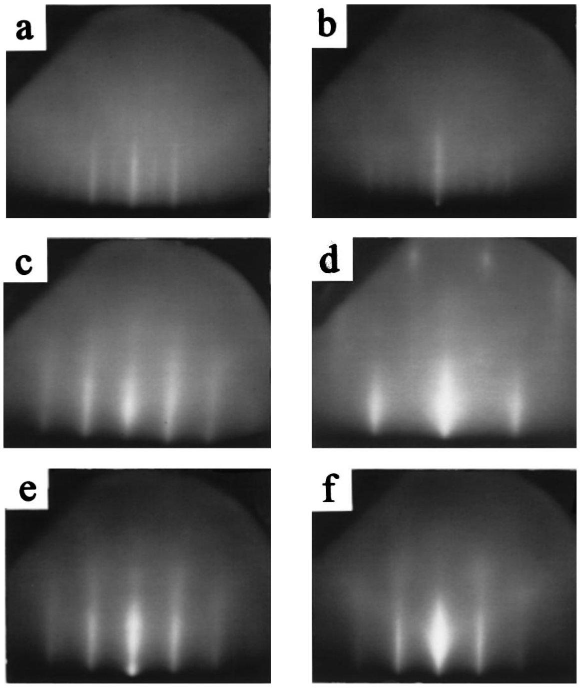

FIG. 2. RHEED patterns of (a) CdTe(111)*A* with Te ML deposition–(110) azimuth, (b) CdTe(111)*A* with Te ML deposition–(112) azimuth, (c) 2 Å Bi–(110) azimuth, (d) 2 Å Bi–(112) azimuth, (e) 10 Å Bi–(110) azimuth, and (f) 50 Å Bi–(110) azimuth.

when using a Te ML. From RBS and reflectance difference spectroscopy (RDS) studies, they showed that Te does not segregate to the growth front but remains near the ZnSe/GaAs interface. On the other hand, the XPS results of other researchers implied that the addition of a Te ML on GaAs(001) suppresses the island growth of $In_xGa_{1-x}As$ and that the Te layer floats on the growth front.[28,29]

Since a surfactant may reside at either the interface or the free surface, the degree of segregation depends on the details of the specific system (and also on the growth kinetics if the system is not fully in equilibrium). There seems to be some tendency in the surface-science community to assume that the action of the surfactant is restricted to the free surface. However, our Bi/CdTe(111)*A* Te surfactant results, as well as those for InAs/GaAs (Ref. 32) and ZnSe/GaAs,[33] would be excluded by such a definition. Reduction of both the surface and interface free energies is generally the driving force for surfactant-mediated growth. However, the strong Te-Cd bonding significantly favors the incorporation of Te at the interface rather than allowing the Te to float to the film surface. Thus by bonding to the substrate, a Te ML on CdTe(111)*A* works as a surfactant primarily by reducing the interface (rather than surface) free energy.

III. Bi/CdTe SUPERLATTICE GROWTH

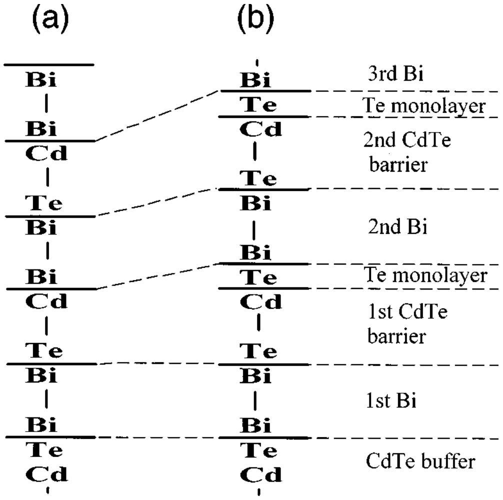

FIG. 3. (a) Bi/CdTe SL structure and (b) the suggested SL structure with Te ML.

Having established that Te interface mediates the layer-by-layer growth of Bi thin films, we next applied this approach to the growth of Bi/CdTe SL's. The growth was initiated with a Bi layer on the CdTe(111)*B* buffer layer, which is known to result in layer-by-layer growth. Our previous RHEED and wet-etching experiments showed that the CdTe growth on Bi starts with a Te layer and ends with Cd.[1] The next Bi layer then ordinarily exhibits 3D island growth if no Te surfactant is employed during the first 50 Å of growth. The schematic of the Bi/CdTe SL structure without a surfactant in Fig. 3(a) shows the polarity inversion of the first CdTe layer and subsequent CdTe layers on Bi. However, Fig. 3(b) shows the SL structure with a Te ML between each Cd-terminated face of CdTe and the subsequent Bi layer. In order to verify the role of the Te ML, two different 30 Å Bi/100 Å CdTe SL's, with and without the Te ML, were grown. The 30 Å Bi thickness was chosen since previous results showed that the initial 3D island growth of Bi on CdTe(111)*A* becomes layer-by-layer on Cd-terminated faces only after 50 Å.

Without the Te ML the streaky RHEED patterns disappeared after several periods, implying that the SL does not grow epitaxially. This is supported by the x-ray diffraction (XRD) patterns for the two SL's, which are shown in Fig. 4. While both XRD scans contain a strong CdTe(111) Bragg peak from the substrate, the absence of SL satellites in the scans for the structure without the Te surfactant is indicative of mixed layers. However, introduction of the Te ML re-

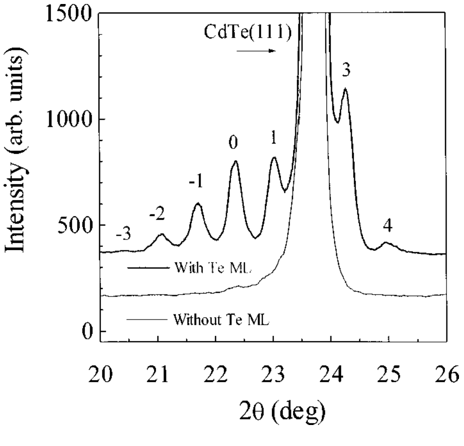

FIG. 4. X-ray diffraction pattern of 50 periods of 30 Å Bi/100 Å CdTe SL's with and without Te ML.

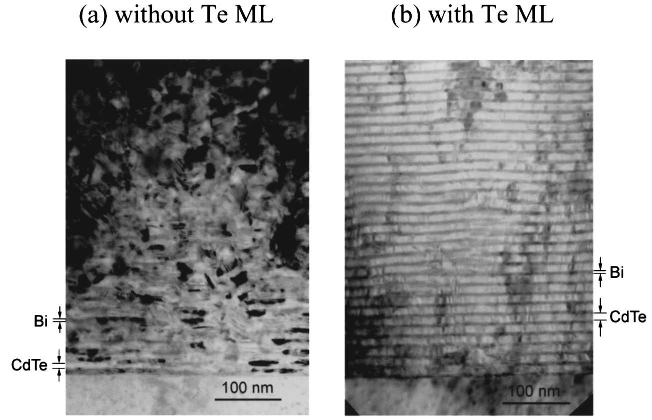
(a) without Te ML (b) with Te ML

FIG. 5. TEM pictures of 50 periods of 30 Å Bi/100 Å CdTe SL's (a) without Te ML and (b) with Te ML.

sulted in a smooth Bi/CdTe SL with well defined layer thickness as shown in Fig. 4. Four orders of satellite reflections can be seen, attesting to the quality of the structure. These results imply that the introduction of Te may allow the growth of SL's with very small Bi well thicknesses.

Figure 5 shows cross-sectional TEM images of the 30 Å Bi/100 Å CdTe SL's with and without the Te ML deposition. Note that without the Te ML, it is difficult to discern the interface after several periods. The growth of large grains along with severe intermixing is observed. However, for the Te atomic layer epitaxy case, a sharp interface was observed over many periods, in agreement with the XRD results. There was no evidence that 3D islands were present when Te ML's were incorporated.

IV. CONCLUSIONS

Our results demonstrate that by introducing a Te ML on the CdTe(111)*A* (Cd-terminated) face, the growth mode of Bi was changed from 3D island to layer-by-layer growth. To our knowledge, this is the first reported surfactant for the Bi/CdTe system. The Te ML remains at the Bi/CdTe(111)*A* interface where it is deposited, similar to systems like ZnSe/GaAs (Ref. 33) and $In_{1-x}Ga_xAs$/GaAs.[28,29] This method is shown to allow the growth of Bi/CdTe SL's with high structural quality, which may be important for a new class of thermoelectric devices. One important aspect of the Te ML incorporated in Bi/CdTe SL's is the possible effect it can have on the electrical properties. This issue will be discussed elsewhere.[37]

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[1] A. DiVenere, X. J. Yi, C. L. Hou, H. C. Wang, J. B. Ketterson, G. K. Wong, and I. K. Sou, Appl. Phys. Lett. **62**, 2640 (1993).

[2] J. A. Venables, G. D. T. Spiller, and M. Hanbucken, Rep. Prog. Phys. **47**, 399 (1984).

[3] C. H. Choi, R. Ai, and S. A. Barnett, Phys. Rev. Lett. **67**, 2826 (1991).

[4] M. Copel, M. C. Reuter, Efthimios Kaxiras, and R. M. Tromp, Phys. Rev. Lett. **63**, 632 (1989).

[5] M. Copel, M. C. Reuter, M. Horn−von Hoegen, and R. M. Tromp, Phys. Rev. B **42**, 11 682 (1990).

[6] K. Fujita, S. Fukatsu, H. Yaguchi, T. Igarashi, Y. Shiraki, and R. Ito, Jpn. J. Appl. Phys., Part 2 **29**, L1981 (1990).

[7] S. Iwanari and K. Takayanagi, Jpn. J. Appl. Phys., Part 2 **30**, L1978 (1990).

[8] J. M. C. Thornton, A. A. Williams, J. E. MacDonald, R. G. van Silfhout, J. F. van der Veen, M. Finney, and C. Norris, J. Vac. Sci. Technol. B **9**, 2146 (1991).

[9] M. Horn−von Hoegen, F. K. LeGoues, M. Copel, M. C. Reuter, and R. M. Tromp, Phys. Rev. Lett. **67**, 1130 (1991).

[10] R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. **68**, 954 (1992).

[11] H. J. Osten, J. Klatt, G. Lippert, B. Dietrich, and E. Bugiel, Phys. Rev. Lett. **69**, 450 (1992).

[12] G. Meyer, B. Voigtlander, and N. M. Amer, Surf. Sci. Lett. **274**, L541 (1992).

[13] G. S. Petrich, A. M. Dabiran, and P. I. Cohen, Appl. Phys. Lett. **61**, 162 (1992).

[14] H. Nakahara and M. Ichikawa, Appl. Phys. Lett. **61**, 1531 (1992).

[15] B. Voigtlander and A. Zinner, Surf. Sci. Lett. **292**, L775 (1993).

[16] D. J. Eaglesham, F. C. Unterwald, and D. C. Jacobson, Phys. Rev. Lett. **70**, 96 (1993).

[17] K. Sakkamoto, K. Kyoya, M. Miki, H. Matsushita, and T. Sakamoto, Jpn. J. Appl. Phys., Part 2 **32**, L204 (1993).

[18] M. Horn−von Hoegen, B. M. Muller, A. Al-Falou, and M. Henzler, Phys. Rev. Lett. **71**, 3170 (1993).

[19] J. Falta, M. Copel, F. K. LeGoues, and R. M. Tromp, Appl. Phys. Lett. **62**, 2962 (1993).

[20] R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. **70**, 966 (1993).

[21] M. Horn−von Hoegen, M. Copel, J. C. Tsang, M. C. Reuter, and R. M. Tromp, Phys. Rev. B **50**, 10 811 (1994).

[22] M. Horn−von Hoegen, B. M. Muller, and A. Al-Falou, Phys. Rev. B **50**, 11 640 (1994).

[23] M. Copel and R. M. Tromp, Phys. Rev. Lett. **72**, 1236 (1994).

[24] P. O. Pettersson, C. C. Ahn, T. C. McGill, E. T. Croke, and A. T. Hunter, Appl. Phys. Lett. **67**, 2530 (1995).

[25] M. Horn−von Hoegen, J. Falta, M. Copel, and R. M. Tromp, Appl. Phys. Lett. **66**, 487 (1995).

[26] M. Katayama, T. Nakayama, M. Aono, and C. F. Mcconville, Phys. Rev. B **54**, 8600 (1996).

[27] J. Falta, T. Schmidt, A. Hille, and G. Materlik, Phys. Rev. B **54**, R17 288 (1996).

[28] N. Grandjean, J. Massies, and V. H. Etgens, Phys. Rev. Lett. **69**, 796 (1992).

[29] J. Massies and N. Grandjean, Phys. Rev. Lett. **48**, 8502 (1993).

[30] S. Higuchi and Y. Nakanishi, J. Appl. Phys. **71**, 4277 (1992).

[31] N. Grandjean, J. Massies, C. Delamarre, L. P. Wang, A. Dubon, and J. Y. Laval, Appl. Phys. Lett. **63**, 66 (1993).

[32] W. N. Rodrigues, V. H. Etgens, M. Sauvage-Simkin, G. Rossi, F. Sirotti, P. Pinchaux, and F. Rochet, Solid State Commun. **95**, 873 (1995).

[33] A. Ohtake, L. H. Kuo, T. Yasuda, K. Kimura, S. Miwa, T. Yao, K. Nakajima, and K. Kimura, J. Vac. Sci. Technol. B **15**, 1254 (1997).

[34] L. D. Hicks, T. C. Harman, and M. S. Dresselhaus, Appl. Phys. Lett. **63**, 3230 (1993).

[35] S. Cho, A. DiVenere, G. K. Wong, J. B. Ketterson, J. R. Meyer, and C. A. Hoffman, Solid State Commun. **102**, 673 (1997).

[36] C. Hsu, S. Sivananthan, X. Chu, and J. P. Faurie, Appl. Phys. Lett. **48**, 908 (1986).

[37] S. Cho, A. DiVenere, G. K. Wong, J. B. Ketterson, J. R. Meyer, and C. A. Hoffman (unpublished).