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Direct Observation of the E_- Resonant State in $GaAs_{1-x}Bi_x$

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Bismuth-derived resonant states with T_2 symmetry are detected in the valence band of $GaAs_{1-x}Bi_x$ using electromodulated reflectance. A doublet is located 42 meV below the valence band edge of GaAs that is split by local strain around isolated Bi impurity atoms. A transition associated with a singlet is also observed just above the GaAs spin orbit split-off band. These states move deeper into the valence band with increasing Bi concentration but at a much slower rate than the well-known giant upward movement of the valence band edge in $GaAs_{1-x}Bi_x$. Our results provide key new insights for clarifying the mechanisms by which isovalent impurities alter the bandstructure of the host semiconductor.

Alloying a compound semiconductor with an isovalent element whose electronegativity and size vary substantially from the host anion substituted is known to produce bound or resonant trap states.[1] Highly electronegative elements, such as N or O, introduce localized A_1-symmetry states near the host conduction band minimum (CBM) that act as electron traps.[1] Larger atoms with low ionization energies, such as Bi or Te, introduce T_2-symmetry states near the valence band maximum (VBM) that act as hole traps.[2] Resonant trap states profoundly influence the alloy bandstructure when they are located in close proximity to either the VBM or CBM of the host. Dilute $GaAs_{1-x}N_x$ presents an archetypal system for investigating this effect, wherein the presence of a N-related resonant state in the conduction band induces a downward shift of the CBM and a consequent giant reduction in the bandgap energy by 180 meV/% N.[3,4,5] The existence of this state was first confirmed experimentally by forcing it into the bandgap with externally applied pressure in nitrogen-doped GaAs:N.[6] Early theoretical calculations suggested that the bandgap reduction was caused by wavefunction localization at the N impurities.[7] Subsequent detection of a resonant state E_+ transition in $GaAs_{1-x}N_x$ alloys by modulated reflectance spectroscopy radically changed the thinking in this field[4,5] and laid the foundation for new but conflicting theoretical models describing the origin of the alloy's unusual behavior. The band anticrossing (BAC) model suggests that the development of the E_+ state and downward shift of the CBM arises through repulsion of the states resulting from the hybridization of the host Γ conduction band states with the N resonant level.[5,8,9,10,11] In contrast, experimental evidence and first principles calculations indicate that the localized N state induces a mixing of many conduction band states.[12,13,14] Despite two decades of research, the mechanisms for the abnormal bandstructure changes remain

unresolved. Investigation of bandstructure modifications by resonant states in the valence band could provide complementary insight needed to elucidate the underlying cause of the abnormal behavior in alloys comprising chemical and size mismatched elements. Yet to date, no such resonant state has been explicitly detected in the valence band of any semiconductor alloy.

Here we present direct experimental evidence for the observation of a p-like Bi-derived resonant state in the valence band of $GaAs_{1-x}Bi_x$ using electromodulated reflectance. A new series of transitions, termed E_- in analogy to the E_+ transition in $GaAs_{1-x}N_x$, are observed just below the VBM of GaAs that move deeper into the valence band as the Bi concentration increases. Assignment of the E_- transitions as originating from a Bi resonant state is confirmed by lowering the absolute position of the VBM through additional alloying with Al, thereby ejecting this level into the gap. The observation of these p-like doublet and singlet resonant states provides significant new insights into the mechanisms by which isovalent impurities alter the bandstructure of the host semiconductor.

Doping GaAs with Bi creates a system complementary to $GaAs_{1-x}N_x$, in which Bi is predicted to introduce a resonant state within the valence band of GaAs.[14,15] Self-consistent pseudopotential based calculations place the energy of this impurity state, E_{Bi}, ~80 meV below the VBM.[14] Alloying with Bi causes the unstrained bandgap $GaAs_{1-x}Bi_x$ to drop by ~88 meV/% Bi.[16] Density functional theory calculations indicate that both the VBM and E_{Bi}

states localize around the Bi impurity, but that localization is stronger for E_{Bi}.[14,15] This strong localization and the evolution of the bandstructure caused by impurity-impurity, host-host, and impurity-host interactions leads to the giant bandgap reduction.[14] Furthermore, at high Bi concentrations, broadening of the impurity level into a band is predicted to cause the VBM to switch from a predominantly host derived state into a predominantly impurity derived state.[14] In contrast, the BAC models based on k·p and tight binding approaches indicate that level repulsion between the Bi impurity and VBM states cause the bandgap reduction.[17,9,10,11] The ability to directly observe the Bi resonant state and monitor its evolution within the alloy bandstructure as a function of Bi concentration would be an important step toward determining which of these frameworks is accurate. The larger deformation potential of the Bi state than the GaAs valence band states precludes the use of pressure to eject it into the bandgap.[14] Hints of a possible Bi resonant state have come recently from pump-probe measurements of a single $GaAs_{1-x}Bi_x$ sample[18], but this approach is complicated by the complex modeling required to extract the level energy, it does not indicate the nature of the state and it does not provide additional information about the systems evolution with composition. Modulated reflectance, on the other hand, is capable of probing all critical point energies and thus determining how a resonant state influences the bandstructure. $GaAs_{1-x}Bi_x$ has previously been measured by contactless electromodulated reflectance or photomodulated reflectance, but these techniques are not capable of inducing a sufficiently strong electric field modulation.[16,17,19] Consequently, no E_- transition analogous to the E_+ transition in $GaAs_{1-x}N_x$ has yet been observed.

We have overcome this problem by using contacted modulated reflectance techniques to effectively drive the electric field in epitaxial $GaAs_{1-x}Bi_x$ layers. Intrinsic $GaAs_{1-x}Bi_x$ films (0.25% to 1.55% Bi) were grown by molecular beam epitaxy on n-type GaAs substrates at temperatures between 270 and 340 °C. A reference GaAs sample was grown at 585 °C. After growth, the $GaAs_{1-x}Bi_x$ samples were annealed for 5 minutes at 550 °C to remove excess Bi on the surface, which builds up during growth and can interfere with electric field modulation. Devices were fabricated for contacted electromodulated reflectance measurements using an optically transparent 10 nm Au front contact. Measurement were performed at room temperature with a frequency of 400 Hz and a bias of ± 0.1 – 0.3 V. Note that this is still in the low field regime. Lineshape fits to the spectra were carried out using the Aspnes third derivative functional form.[20] Bi-doped ($<10^{18}$ cm^{-3}) $Al_xGa_{1-x}As$ samples (x = 0.30 and 0.33) were used to confirm the position of E_{Bi}, where E_{Bi} was ejected into the gap due to the lower VBM of $Al_xGa_{1-x}As$ compared to GaAs using photoluminescence (PL) measurements at 7 K with a 532 nm laser.

Figure 1 displays modulated reflectance spectra of several $GaAs_{1-x}Bi_x$ samples. The E_0 transition associated with the fundamental bandgap decreases in energy with increasing Bi concentration. Epitaxial dilute bismide layers are known to be resistant to strain relaxation[21], and strain splitting of the heavy hole (HH) and light hole (LH) valence band states has been observed in $GaAs_{1-x}Bi_x$ films with up to 10.4% Bi.[22] The spectra of our samples are similar to previously published data, and accordingly, we have fit the E_0 related features with two transitions.[16,22] Both the energy shift and strain splitting of these

transitions follow the well-established trends in the literature.[16,22] The higher-lying feature, marked $E_0 + \Delta_0$, is associated with the transition from the conduction band to the spin-orbit split-off valence band in the $GaAs_{1-x}Bi_x$ film. The composition dependence of this transition also follows the known trend reported in the literature.[17,22,23] Modulated reflectance spectra of $GaAs_{1-x}Bi_x$ presented in previous reports showed no features between the E_0 and $E_0 + \Delta_0$ transitions.[16,17,19,22] However, the spectra in Fig. 1 clearly exhibit an intermediate feature, labeled *E_*, immediately above GaAs-related E_0 transition that is not present in the GaAs sample. This new transition is distinct in the sample with 0.25% Bi and increases in energy and intensity with increasing Bi concentration. Above this Bi concentration, *E_* splits into two clearly defined transitions, which are labeled *E_ (HH)* and *E_ (LH)*. Finally, a third transition, labeled *E_ (SO),* just above the $GaAs_{1-x}Bi_x$ $E_0 + \Delta_0$ transition is also observed. These transition energies are shown in Fig. 2.

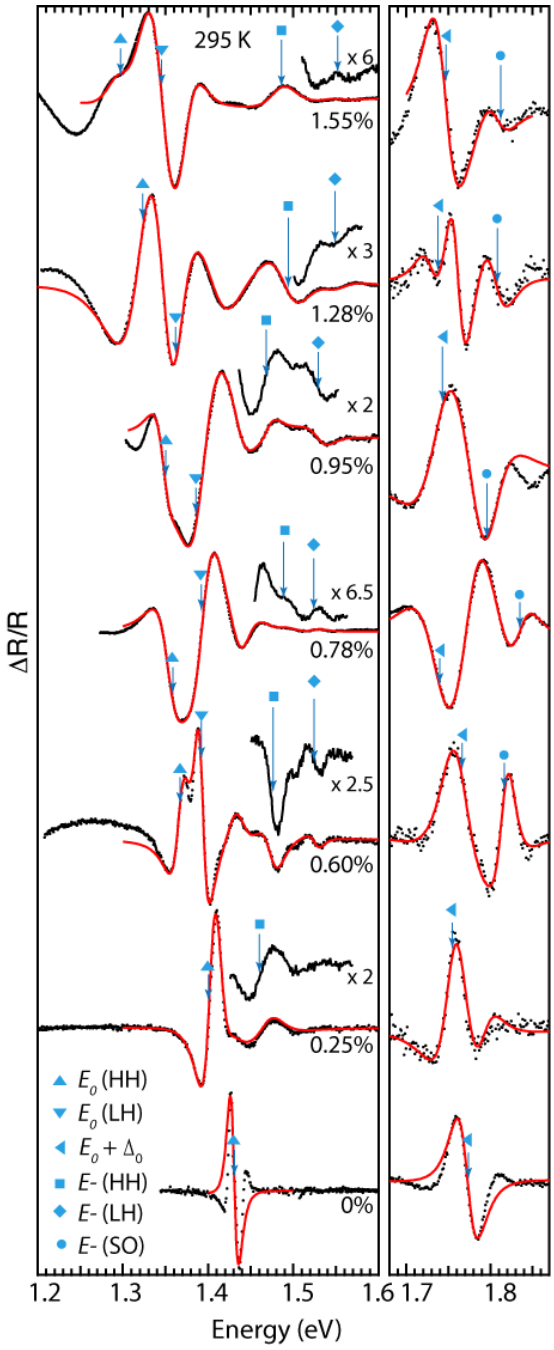

Fig. 1 (Color online) Electromodulated reflectance spectra of $GaAs_{1-x}Bi_x$ samples with Bi concentrations up to 1.55% Bi. The actual data are shown as the dotted lines and the fits to the spectra are show as solid red lines. The transition energies extracted from the fitting process are marked on the spectra with symbols (see legend). Magnified portions of the spectra are also included to clearly show the E_- transitions.

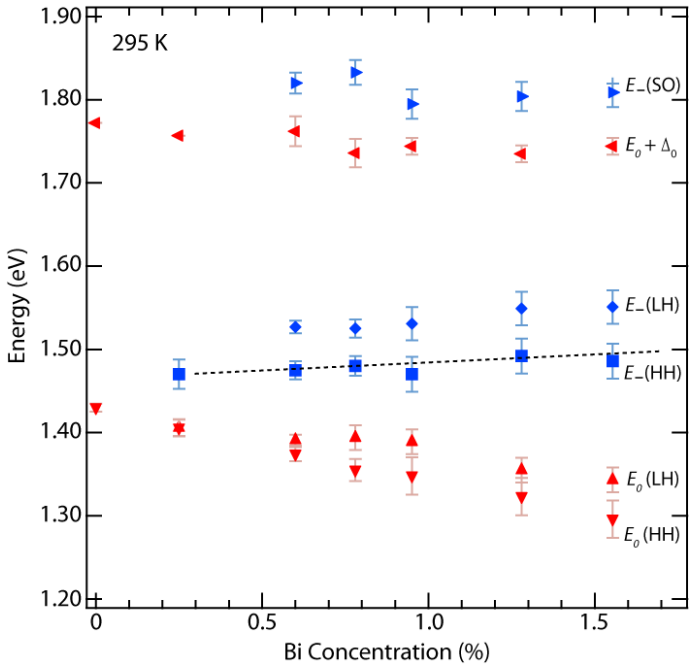

Fig. 2 (Color online) Energies extracted by fitting the electromodulated reflectance transitions presented in Fig. 1. The dashed line is a linear fit to the *E_ (HH)* data.

In Fig. 2, the linear fit to the *E_ (HH)* trend extrapolates to an energy of approximately 1.466 eV at $x = 0$. Considering that E_0^{GaAs} = 1.424 eV at room temperature, this experimental value is separated from E_0^{GaAs} by ~ 42 meV and corresponds to the calculated E_{Bi} level ~ 80 meV below the GaAs VBM.[14] To confirm that the *E_* transition originates from E_{Bi}, we ejected it into the bandgap by alloying the GaAs host with Al, which increases the bandgap by raising the CBM and lowering the VBM by a ratio of ~ 63/37.[24,25] Based on the model of deep trap states in Ref. 1, we assume that E_{Bi} remains relatively stationary with small changes in the host band edges.[1] It should therefore become bound at moderate Al concentrations, as depicted in Fig. 3a. We detected this bound state by low temperature PL in Bi-doped $Al_xGa_{1-x}As$. Figure 3b displays the 7 K PL spectrum of

$Al_{0.30}Ga_{0.70}As$. The feature at 1.932 eV is associated with the donor bound exciton (*BE*) in the host. The expected energy of the bound E_{Bi} state can be calculated by adding the alloying-induced CBM shift and the offset of E_{Bi} from the GaAs VBM (i.e. 42 meV) to the bandgap of GaAs (see Fig. 3a). Using a donor binding energy of 13 meV[26] to determine the actual bandgap of the host, the CBM shift of this sample with respect to GaAs is 259 meV, placing the predicted PL transition associated with E_{Bi} at ~1.820 eV. This is close to the actual peak, marked A_{Bi}, which is assigned to the *A*-line of the bound E_{Bi} state. This transition is broadened by alloy fluctuations in the low temperature grown $Al_{0.30}Ga_{0.70}As$ host. The additional feature on the low energy side of A_{Bi} is typical of that observed in Bi-doped GaP and could consist of broadened phonon replicas or defects.[27] Upon increasing the Al concentration to 33%, the *BE* transition shifts correspondingly (see Fig. 3c), but A_{Bi} does not change substantially.

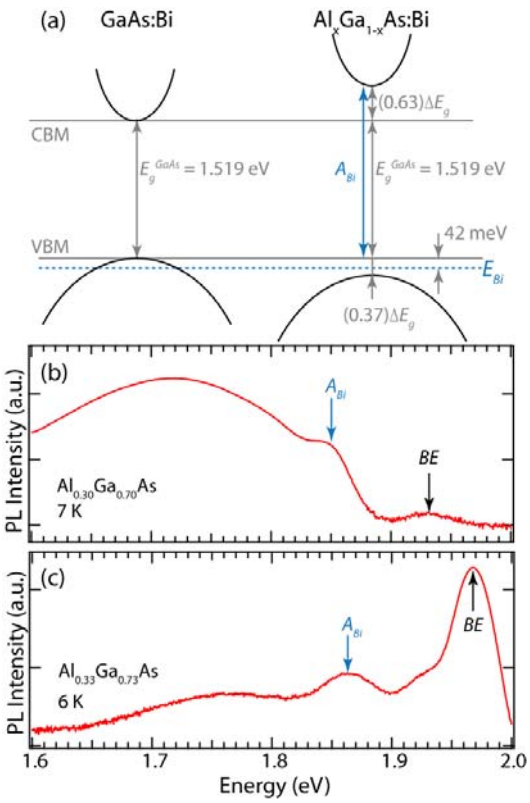

Fig. 3 (Color online) (a) Diagram of GaAs and $Al_xGa_{1-x}As$ CBM and VBMs and the E_{Bi} state at low temperature. The arrow labeled A_{Bi} marks the energy of the expected PL transition from the bound Bi state in $Al_xGa_{1-x}As$. (b) 7 K PL spectrum of a Bi-doped $Al_{0.30}Ga_{0.70}As$ sample and (c) 6K PL spectrum of a Bi-doped $Al_{0.33}Ga_{0.67}As$ sample. Peaks related to the bound exciton, *BE*, and A_{Bi} are marked.

The key result of our modulated reflectance measurements is the observation of three new transitions related to the resonant Bi state in GaAs. Strain-splitting of the $E_0(HH)$ and $E_0(LH)$ transitions suggests that the Bi-derived states will also be strain-split into $E\_(HH)$ and $E\_(LH)$ levels. We find that the $E\_(HH)$ and $E\_(LH)$ splitting differs from the $E_0(HH)$ and $E_0(LH)$ splitting. Theoretically, strain-induced splitting of these states is possible since the T_2 symmetric E_{Bi} triplet state is composed of *p*-like doublet and singlet states when split by the spin-orbit interaction.[14] The large size of the Bi atom exerts a

strong local distortion of the bonds in its immediate vicinity, leading to a locally higher strain field.[14,22,28,29] This strain will therefore lift the degeneracy of the doublet and produce independent HH-like and LH-like transitions in the modulated reflectance spectra. To estimate the localized strain, we calculated the distorted Ga-As (r'_{GaAs}) and Ga-Bi (r'_{GaBi}) bond lengths in a pseudomorphically strained $GaAs_{1-x}Bi_x$ film according to the approach of Woicik, *et al.* [29] using unstrained lattice constants of a_{GaAs} = 5.653 Å and a_{GaBi} =6.324 Å for GaAs and GaBi,[30] respectively, and a bond length of $r = \sqrt{3}/4a$, r'_{GaAs} = 2.4477 Å and r'_{GaBi} = 2.665 Å for 2% Bi. The strain at the Ga-As bonds is roughly equivalent to that of the pseudomorphically strained film[22] (~ 0.26%). Yet the local strain around the Ga-Bi bonds is as high as 8% and does not vary substantially over the dilute Bi concentration studied here. While the deformation potential for the Bi-derived delocalized state is unknown, the locally higher strain around the Ga-Bi bonds accounts for the greater splitting between the E_- states compared to the E_0 states.

The position of the E_- *(SO)* transition suggests that it is associated with the singlet of the E_{Bi} state. Localization of the host valence band states at the Bi atoms accounts for its proximity to the $E_0 + \Delta_0$ transitions.[14] The energy of E_- *(SO)* follows the same trend with composition as the E_- *(HH)* and E_- *(LH)* doublet transitions, further confirming that they are associated with Bi impurities.

Observation of p-like doublet and singlet states associated with the resonant Bi level in GaAs provides clues on how deep isoelectronic impurity states evolve as a result of

alloying. The trend in the $E_{-}(HH)$ and $E_{-}(LH)$ transition energies with composition in Fig. 2 does not match the theoretically expected dependence calculated with the refined BAC model, which determined that the resonant Bi level shifts deeper into the GaAs valence band by ~50 meV over the composition range 0 - 0.5% Bi for a total shift in this composition range of ~100 meV/%Bi.[10] The E_{-} (HH) transition measured here shifts by only 18 meV/% Bi. This behavior is also much different from that of $GaAs_{1-x}N_x$, where the E_{+} transition moved at a similar rate to that for the bandgap.[4,5] Such inconsistencies cast serious doubts about the validity of the often-cited BAC models used to describe the abnormal behavior of dilute nitride and bismide alloys. Our results instead suggest that the Bi resonant levels develop a significant density of states at the cost of the host valence band states, which is reflected in the intensification of the E_{-} transitions with increasing Bi concentration. This suggests a mixing mechanism involving many more bands[14] than accounted for in the BAC framework. Indeed calculations using a self-consistent pseudopotential-based charge patching approach indicate that the Bi-derived resonant state is composed of bulk states from different k points, but predominantly from (1/n, 1/n, 0) k_0 along the Σ line, (1/n, 1/n, 1/n) k_0 along the Λ line, (1/n, 1/n, 0) k_0 along the Δ line, and the Γ point.[14] The involvement of many host bands in the evolution of the resonant Bi-derived states is also consistent with the earlier viewpoint that true deep traps couple to distant energy bands.[1] These insights should be invaluable for understanding the origins of the abnormal behavior of alloys with size-mismatched isoelectronic impurities.

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References

[1] H.P. Hjalmarson, P.Vogl, D.J. Wolford and J.D. Dow, *Phys. Rev. Lett.*, **44**, 810 (1980)

[2] H.P. Hjalmarson, Ph.D. thesis, University of Illinois, 1979 (unpublished)

[3] M. Weyers, M. Sato and H. Ando, *Jpn. J. Appl. Phys.*, **31**, 853 (1992)

[4] J.D. Perkins, A. Mascarenhas, Y. Zhang, J.F. Geisz, D.J. Friedman, J.M. Olson and S.R. Kurtz, *Phys. Rev. Lett.*, **82**, 3312 (1999)

[5] W. Shan, W. Walukiewicz, J.W. Ager, E.E. Haller, J.F. Geisz, D.J. Friedman, J.M. Olson and S.R. Kurtz, *Phys. Rev. Lett.*, **82**, 1221 (1999)

[6] D.J. Wolford, J.A. Bradley, K. Fry and J. Thompson, in *Proceedings of the 17th International Conference on the Physics of Semiconductors,* edited by J.D. Chadi and W.A. Harrison (Springer, New York, 1985)

[7] L. Bellaiche, S.-H. Wei and A. Zunger, *Phys. Rev. B*, **56**, 10233 (1997)

[8] J. Wu, W. Walukiewicz and E.E. Haller, *Phys. Rev. B* **65**, 233210 (2002)

[9] E.O. OReilly, A. Lindsay, P.J. Klar, A. Polimeni and M. Capizzi, *Semicond. Sci. Technol.*, **24**, 033001 (2009)

[10] M. Usman, C.A. Broderick, A. Lindsay and E.P. O'Reilly, *Phys. Rev. B*, **84** 245202 (2011)

[11] C.A. Broderick, *et al.*, *Semicond. Sci. Technol.***, 28**, 125025 (2013)

[12] A. Mascarenhas, M.J. Seong, S. Yoon, J.C. Verley, J.F. Geisz and M.C. Hanna, *Phys. Rev. B*, **68**, 233201 (2003)

[13] P.R.C. Kent and A. Zunger, *Phys. Rev. B*, **64**, 115208 (2001)

[14] Y. Zhang, A. Mascarenhas and L.-W. Wang, *Phys. Rev. B*, **71**, 155201 (2005)

[15] H.-X. Deng, J. Li, S.-S. Li, H. Peng, J.-B. Xia, L.-W. Wang, S.-H. Wei, *Phys. Rev. B*, **82**, 193204 (2010)

[16] S. Francoeur, M.-J. Seong, A. Mascarenhas, S. Tixier, M. Adamcyk and T. Tiedje, *Appl. Phys. Lett.*, **82**, 3874 (2003)

[17] K. Alberi, O.D. Dubon, W. Walukiewicz, K.M. Yu, K. Bertulis and A. Krotkus, *Appl. Phys. Lett.*, **91**, 051909 (2007)

[18] R.S. Joshya, A.J. Ptak, R. France, A. Mascarenhas and R.N. Kini, *Phys. Rev. B*, **90**, 165203 (2014)

[19] L. Bhusal, A.J. Ptak, R. France and A. Mascarenhas, *Semicond. Sci. Technol.*, **24**, 035018 (2009)

[20] D.E. Aspnes, *Surf. Sci.*, **37**, 418 (1973)

[21] R. France, C.-S. Jiang and A.J. Ptak, *Appl. Phys. Lett.*, **98**, 101908 (2011)

[22] Z. Batool, K. Hild, T.J.C Hosea, X. Lu, T. Tiedje and S.J. Sweeney, *J. Appl. Phys.*, **111**, 113108 (2012)

[23] B. Fluegel, S. Francoeur, A. Mascarenhas, S. Tixier, E.C. Young and T. Tiedje, *Phys. Rev. Lett.*, **97**, 067205 (2006)

[24] T.W. Hickmott, P.M. Solomon, R. Fischer and H. Morkoc, *J. Appl. Phys*., **57**, 2844 (1985)

[25] M.O. Watanabe, J. Yoshida, M. Mashita, T. Nakanisi and A. Hojo, *J. Appl. Phys.*, **57**, 5340 (1985)

[26] D.A. Beaton, K. Alberi, B. Fluegel, A. Mascarenhas and J.L. Reno, *Appl. Phys. Express*., **6**, 071201 (2013)

[27] P.J. Dean, J.D. Cuthbert and R.T. Lynch, *Phys. Rev.*, **179**, 754 (1969)

[28] T.N. Morgan and H. Maier, *Phys. Rev. Lett.*, **27**, 1200 (1971)

[29] J.C. Woicik, J.G. Pellegrino, B. Steiner, K.E. Miyano, S.G. Bompadre, L.B. Sorensen, T.-L. Lee and S. Khalid, *Phys. Rev. Lett.*, **79**, 5026 (1997)

[30] A. Janotti, S.-H. Wei and S.B. Zhang, *Phys. Rev. B*, **65**, 115203 (2002)