Raman study of an electric-field-induced phase transition in $Pb(Zn_{1/3}Nb_{2/3})O_3$-8%$PbTiO_3$

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Electric-field-induced structural transition of a single crystal $Pb(Zn_{1/3}Nb_{2/3})O_3$-8%$PbTiO_3$ grown in the (001) direction was studied by use of Raman scattering spectroscopy. By comparing the changes in Raman spectra induced by the electric field with the temperature-dependent changes, we could confirm that the structural transition to tetragonal phase is initiated at a threshold electric field E_{c1} and completed at higher transition field E_{c2}. In the electric-field range from E_{c1} to E_{c2}, it is found that rhombohedral and tetragonal phases coexist. The lower threshold field E_{c1} is found to coincide with the field at which the strain rises abruptly in the strain electric-field hysteresis loop while the upper threshold field E_{c2} corresponds to the electric field where a slope change is observed in the high-field saturation region beyond the hysteresis loop.

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I. INTRODUCTION

Since the 1960s many research workers have been interested in the mixed perovskite-type ferroelectrics $A(B_IB_{II})O_3$, where A site ions are Pb ions and B sites are occupied by two different ions of various combinations satisfying the effective chemical valency of $+4$. These pseudocubic or rhombohedral compounds tend to become ferroelectric relaxors and transform to relaxor-based tetragonal ferroelectrics when $PbTiO_3$ (PT) is doped in high concentration.[1] These relaxor-based ferroelectric materials are found to have very large piezoelectric and dielectric constants near the morphotrophic phase boundaries (MPB), and have drawn great concern of many research works for actuators and sensor applications.[2]

Lead zinc niobate $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) is a ferroelectric relaxor characterized by a broad and frequency-dependent diffused phase transition, whereas PT is a normal ferroelectric crystal of tetragonal symmetry with space group $P4mm$ at room temperature. The solid solution $(1-x)$PZN-xPT (PZN-xPT) has the MPB in the range of PT concentration from $x=9.0\%$ to $x=9.5\%$ at room temperature and can be grown to a single crystal[3] in contrast to the case of ceramic PZN relaxors. Recently $Pb(Zn_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PZN-xPT) crystals have received a great attention after the discovery of a giant piezoelectricity in this relaxor-based ferroelectric single crystal PZN-xPT of $x=8\%$.[4] PZN-xPT shows a structural phase transition from the low-temperature rhombohedral phase to the high-temperature tetragonal phase, where the phase-transition temperature depends on the mixing concentration x of PT.[3,5] In the rhombohedral PZN-xPT crystal with the spontaneous polarization along the (111) direction, the electric field along the (001) direction gives rise to the giant piezoelectric response, whereas a field along the (111) direction gives a normal small strain.[4] The origin of this giant piezoelectricity observed in the PZN-8%PT single crystal was suggested as due to a polarization rotation in the field-induced phase transition from the rhombohedral phase of a low-level strain to the tetragonal phase of a high-level strain.[4,6]

In the present experimental work, we measured Raman spectra of a single crystal of PZN-8%PT under various electric fields in the (001) direction in the hope for a better understanding of the structural phase transition associated with the giant piezoelectricity. PZN-8%PT grown in the (001) direction is found to have a larger piezoelectric constant than PZN-9.5%PT which is closer to the MPB concentration.[4] Raman-scattering spectra of both ferroelectric relaxors[7] and relaxor-based ferroelectrics[8,9] with B-site ions of $+2$ and $+5$ valencies in $A(B_IB_{II})O_3$ perovskites has been studied in great detail but only for temperature-dependent changes associated with the structural phase transitions. Previous Raman results show that, even in the high-temperature cubic phase, the Raman spectra do not differ qualitatively from those of rhombohedral phase except in the intensities of various modes. This was taken as the evidence for existence of microdomains of different polarizations even in the cubic phase with a built-in disorder of the B-site ions.[9] However, the effects of electric fields on the polar microdomains and thus the structural changes have not been studied yet by Raman spectroscopy, which may offer detailed information about the field-induced structural changes associated with the giant piezoelectricity. Our Raman scattering study of PZN-8%PT single crystal clearly shows that the electric field applied in the (001) direction induces a phase transition from the rhombohedral at low fields to the tetragonal phase at high fields through a phase coexistence region in the intermediate fields.

II. EXPERIMENT

Single crystals of PZN-8%PT solid solution were grown by the high-temperature flux method.[4] Pseudocubic crystal axes were determined by a Laue diffraction pattern, and the

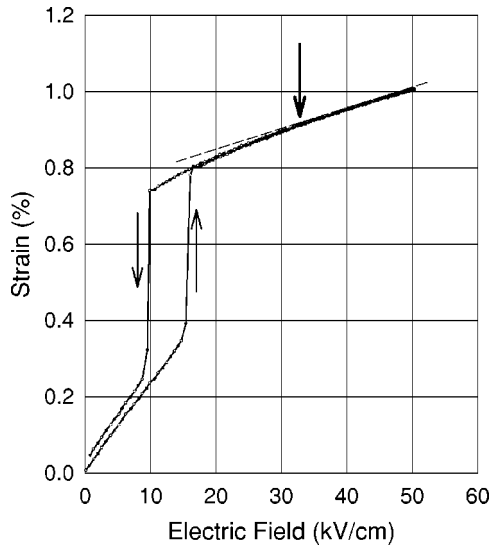

FIG. 1. Longitudinal strain of the PZN-8%PT crystal in the (001) direction as a function of the electric field (kV/cm) applied along the (001) direction at room temperature (22.5. °C). The thick arrow indicates an inflection point in the electric-field strain curve.

crystal was cut into slices in the (001) direction. The (001) surfaces of the thin-film samples were carefully polished before coating electrodes on the two surfaces. Indium-tin-oxide (ITO) transparent electrode was coated on one side and gold electrode on the other side of the crystalline sample, and Raman signals of the samples were taken through the ITO electrodes. The ITO electrode has no Raman active mode and does not interfere with Raman spectra of the sample beneath it.

Raman spectra were taken using an Ar-ion laser operated at the 514.5-nm line. Scattered light was collected by an ULWD lens ($\times 20$) system in the backscattering geometry. A triple grating spectrometer with a charge-coupled device (CCD) detector (Jobin Yvon T64000) was employed to reduce the stray light background in the low-frequency Raman spectra. Raman spectra were measured in two different scattering geometries; parallel (VV) and cross (VH) scattering geometries. In the parallel scattering geometry, the polarizations of the incident and the scattered light are both in the (100) direction. In the cross scattering geometry, the polarization of the incident light is in the (100) direction and that of the scattered light in the (010) direction. The PZN-8%PT samples studied in this work have thickness of about 0.11 mm. The external electric field was applied in the (001) direction through the transparent ITO electrode in the range of 0–45 kV/cm and temperature of the sample was varied from the room temperature to well above the transition temperature. A *K*-type thermocouple was used to measure temperature of the sample surface where Raman signals were collected.

III. RESULTS AND DISCUSSION

As can be seen in Fig. 1 of the electric-field strain curve of the PZN-8%PT crystal in the (001) direction, a rapid increase of strain beyond a normal piezoelectric limit appears

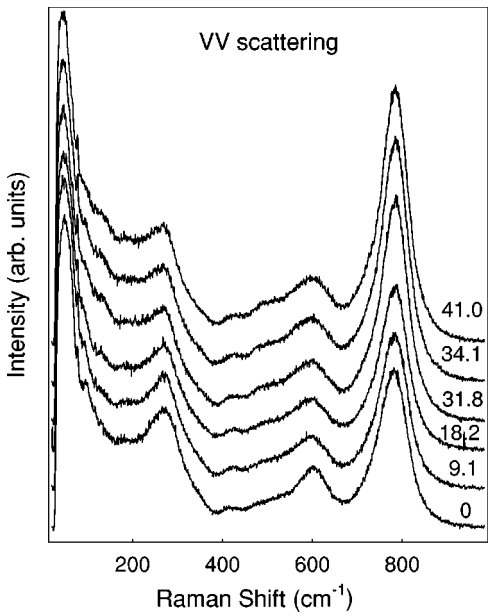

FIG. 2. Room-temperature (22.5 °C) Raman spectra of the PZN-8%PT crystal at various electric fields (kV/cm) applied in the (001) direction in the parallel (VV) scattering geometry. Each spectrum is shifted by constant amount in intensity for clarity.

at a threshold field strength of 15–17 kV/cm (denoted as E_{c1}) as the field strength increases. Park and Shrout[4] suggested a phase transition from the rhombohedral to the tetragonal structure at this value of the applied field. At a stronger field (marked by an arrow in the figure) beyond the hysteresis loop, we notice that there exists a slope change in the electric-field strain curve. The slope change indicates that there might be a change in the structural properties at this particular electric field, and indeed, it is observed in our current Raman study. We denote this particular field as E_{c2}.

We measured Raman spectra of the PZN-8%PT crystal under electric fields applied in the (001) direction up to 45 kV/cm to elucidate the details of the field-induced structural phase transition. Figures 2 and 3 show the Raman spectra of the PZN-8%PT taken at room temperature (22.5 °C) at several selected values of the applied electric field. From Raman spectra in the parallel polarization scattering geometry (Fig. 2), we observe that the Raman modes near 100 and 780 cm^{-1} increase in intensity when the applied electric field is increased. On the other hand, in the cross polarization scattering geometry (Fig. 3), Raman modes near 100, 600, and 780 cm^{-1} are seen to decrease in intensity as the applied field is increased. The Raman mode at 270 cm^{-1}, however, is seen to remain unchanged in both Figs. 2 and 3, which can be taken as a reference mode for a quantitative comparison of the field-induced changes of the different modes.

When the applied electric field reaches 18.2 kV/cm, the relative intensities of the Raman modes at 100, 600, and 780 cm^{-1} with respect to that of the 270-cm^{-1} mode are observed to make an abrupt change. Note that 18.2 kV/cm is just above the threshold field E_{c1} in the electric-field strain curve of Fig. 1. Further increase of the electric field brings about another notable change in the relative intensities of the

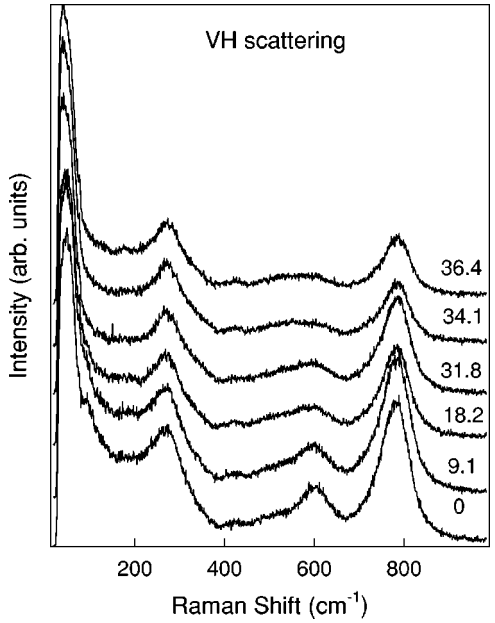

FIG. 3. Room temperature (22.5 °C) Raman spectra in the cross (VH) scattering geometry at various electric fields (kV/cm). Each spectrum is shifted by constant amount in intensity for clarity.

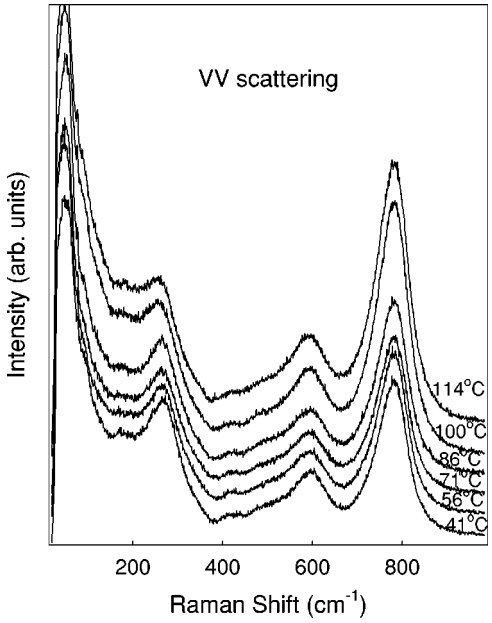

FIG. 5. Raman spectra of the PZN-8%PT crystal at various temperatures in the parallel (VV) scattering geometry. Each spectrum is shifted by constant amount in intensity for clarity.

Raman modes at 100, 600, and 780 cm^{-1} with respect to the mode at 270 cm^{-1} as the applied field reaches 34.1 kV/cm. These changes are readily seen in Fig. 4, where the ratio of the cross component to the parallel component of 100- (circle), 600- (triangle), and 780- (square) cm^{-1} modes are plotted as functions of the applied electric field. The vertical lines are drawn at the values of the E_{c1} and E_{c2} which were determined from the electric-field strain curve (Fig. 1). From Fig. 4, we notice that the relative intensities are changing almost linearly with the change of the electric fields between E_{c1} and E_{c2}. Below E_{c1} and above E_{c2}, the relative intensities stay nearly constant. Clearly there is a strong correlation between E_{c1} and E_{c2} determined from the electric-field strain curve and those determined from the changes in the relative Raman intensities of the 100-, 600-, and 780-cm^{-1} modes. We do believe that these changes are due to structural phase transitions as confirmed from the following temperature-dependent Raman spectroscopy.

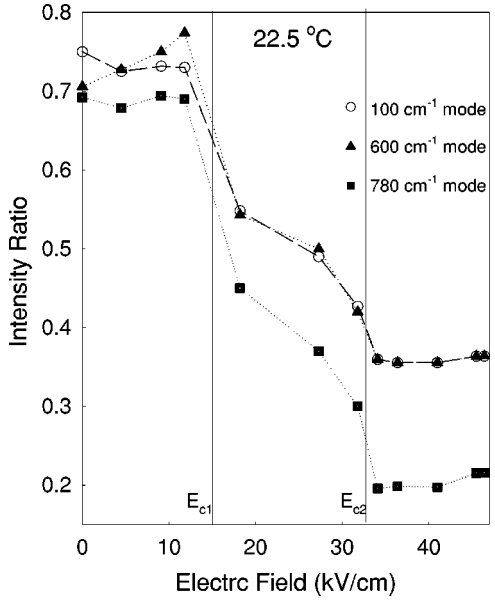

FIG. 4. Intensity ratio of the cross component to the parallel component of the 100-cm^{-1}(circle), 600-cm^{-1}(triangle), and 780-cm^{-1}(square) modes as functions of the applied electric fields (kV/cm).

The structure of PZN-8%PT is known to be rhombohedral at room temperature, and becomes tetragonal at $T \geqslant 100$ °C (see Fig. 5 of Ref. 3).[3,5] Figures 5 and 6 show our own Raman spectra of PZN-8%PT at various temperatures in the parallel (VV) and the cross (VH) scattering geometries, respectively. At low temperatures, the Raman spectra in the parallel scattering geometry are similar to those in the cross scattering geometry. However, at temperatures above 100 °C, the Raman spectra in the parallel scattering geometry are distinguished from those in the cross scattering geometry. The three modes at 100, 600, and 780 cm^{-1} show abrupt changes in intensity above 100 °C, which is known to be the critical temperature of the structural phase transition from the rhombohedral to the tetragonal structure.[3,5] In a previous Raman measurement[9] on a (001)-oriented PZN-9%PT at various temperatures, the Raman spectra were almost identical to each other with a change only in the polarization ratio of the 780-cm^{-1} mode upon the phase transition. Apparently, the PZN-8%PT single crystal is exhibiting stronger contrast than PZN-9%PT in changes of the Raman spectra upon the structural phase transition.

Note that all the Raman modes observed in the rhombohedral phase are also present in the tetragonal phase despite the large changes in their intensities. In addition, all the modes appear both in the parallel and cross scattering geom-

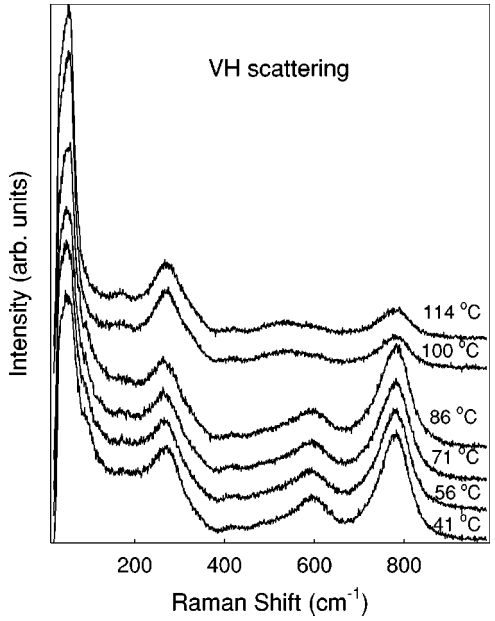

FIG. 6. Raman spectra of the PZN-8%PT crystal at various temperatures in the cross (VH) scattering geometry. Each spectrum is shifted by constant amount in intensity for clarity.

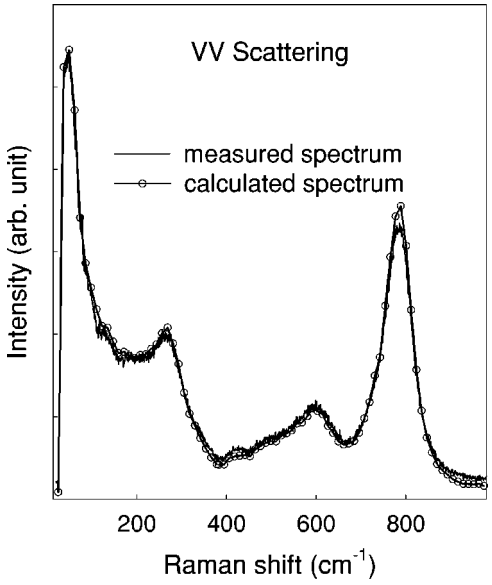

FIG. 7. Calculated Raman spectra in comparison with the observed Raman spectra of the PZN-8%PT crystal at one arbitrary intermediate electric field of 27.3 kV/cm in the parallel (VV) scattering geometry. Details of calculation are in the text.

etries. A strict selection rule should apply to the appearance (or disappearance) of Raman modes for single crystals of single domain so that one should expect a complete extinction of certain Raman modes upon the structural phase transition. However, our Raman results of PZN-8%PT single crystal as well as previous Raman results of PZN-9%PT single crystal do show incomplete selection rules of the observed Raman modes. This effect of apparent symmetry breaking may be due to, and thus may serve as an evidence for, the existence of the micropolar domains in the single crystal of PZN-x%PT.

We note that the changes observed in the zero-field Raman spectra across the critical temperature in the temperature dependence measurements (Figs. 5 and 6) are significant and comparable to the changes observed in the room-temperature Raman spectra across the upper transition field E_{c2} in the electric-field dependence measurements (Figs. 2 and 3). On the other hand, the changes in the Raman spectra across E_{c1} are not as obvious as those across E_{c2}. This suggests that the field-induced phase transition from the rhombohedral to the tetragonal phase is completed at the fields above E_{c2}, not E_{c1}. This is in contrast to the earlier interpretation made by Park *et al.*, who suggested that the phase transition would occur at E_{c1} from their x-ray-diffraction measurements under electric field.[5] The lower critical field E_{c1}, at which rapid increase of strain beyond a normal piezoelectric limit appears in the electric-field strain curve (Fig. 1), may be the field at which the field-induced phase transition is initiated.

In fact, Fig. 4 supports that the field-induced phase transition is initiated at E_{c1} and completed at E_{c2}. In the figure, the depolarization ratios of the 100-, 600-, and 780-cm^{-1} modes remain constant below E_{c1}, decrease almost linearly as the electric fields increase above E_{c1}, and then saturate to constant values above E_{c2}. This figure suggests that, in the intermediate range of the electric fields between E_{c1} and E_{c2}, the phase of the PZN-8%PT is actually a mixture of the rhombohedral and the tetragonal phases but not a third phase. Assume that the mixing ratio of the two phases at an intermediate electric field (EI) are proportional to the difference from the E_{c1} with respect to the difference of the two critical fields $E_{c2}-E_{c1}$. Then one would expect that the Raman spectra at the electric fields of the intermediate range could be represented by a linear superposition of the Raman spectrum at below E_{c1} and the Raman spectrum at above E_{c2}. In Figs. 7 and 8, we present the calculated Raman spec-

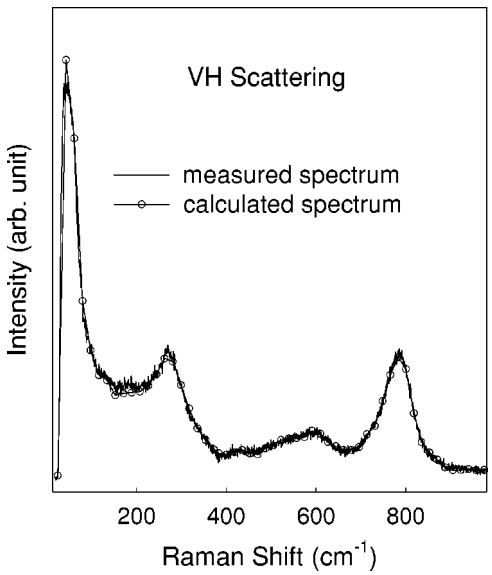

FIG. 8. Calculated Raman spectra in comparison with the observed Raman spectra of the PZN-8%PT crystal at 27.3 kV/cm in the cross (VH) scattering geometry.

tra in the parallel and the cross scattering geometries, respectively, at an intermediate electric field of 27.3 kV/cm in comparison with the observed Raman spectra at the same field. The calculated spectra was obtained from the linear superposition of the Raman spectra at E_{c1} and E_{c2},

$$\{\mathrm{CAL}\}=[r\times\{\mathrm{RHS}\}+(1-r)\times\{\mathrm{TGS}\}],$$

where {CAL} represents the calculated Raman spectra, $r=(E_{c2}-EI)/(E_{c2}-E_{c1})$, EI an intermediate electric field between E_{c1} and E_{c2} (27.3 kV/cm in this case), {RHS} Raman spectrum of the rhombohedral phase, and {TGS} Raman spectrum of the tetragonal phase. The agreement between the experimental and the calculated Raman spectra is excellent for both parallel and cross scattering geometries, which strongly suggests the coexistence of the rhombohedral and tetragonal phases in the intermediate field region (16–33 kV/cm).

There exists an attempt to show a direct evidence for the structural transition in PZN-8%PT under electric field in the (001) direction using an x-ray-diffraction (XRD) method.[10] The measured value of the lattice parameter c at the highest available electric field of their experiment was even smaller than the value of the PZN-12%PT sample which is tetragonal at room temperature.[10] This indicates that their maximum applied electric field was just above E_{c1}, but less than E_{c2}.

IV. CONCLUSION

We have examined the electric-field-induced structural phase transition in the PZN-8%PT single-crystal samples using Raman spectroscopy. Our Raman study shows that, in the PZN-8%PT single crystal under electric field in the (001) direction, the structural transition from the rhombohedral phase to the tetragonal phase is initiated at E_{c1} (15–17 kV/cm), and completed at E_{c2} (about 33 kV/cm). In the intermediate electric fields between E_{c1} and E_{c2}, both the rhombohedral and the tetragonal phases coexist in the PZN-8%PT single crystal.

ACKNOWLEDGMENTS

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[1] H. Ouchi, K. Nagano, and S. Hayakawa, J. Am. Ceram. Soc. **48**, 169 (1965).
[2] L. E. Cross, in *Fundamental Physics of Ferroelectrics 2000 (AIP CP-535)*, edited by R. E. Cohen (American Institute of Physics, Melville, NY, 2000).
[3] Jun Kuwata, Kenji Uchino, and Shoichiro Nomura, Ferroelectrics **37**, 579 (1981).
[4] Seung-Eek Park and Thomas R. Shrout, J. Appl. Phys. **82**, 1804 (1997).
[5] Maureen L. Mulvihill, Seung-Eek Park, George Risch, Zhuang Li, Kenji Uchino, and Thomas R. Shrout, Jpn. J. Appl. Phys., Part 1 **38**, 3984 (1996).
[6] H. Fu and R.E. Cohen, Nature (London) **403**, 281 (2000).
[7] H. Ohwa, M. Iwata, N. Yasuda, and Y. Ishibashi, Jpn. J. Appl. Phys., Part 1 **37**, 5410 (1998).
[8] Heike Idink and William B. White, J. Appl. Phys. **76**, 1789 (1994).
[9] Fuming Jiang and Kojima, Jpn. J. Appl. Phys., Part 1 **38**, 5128 (1999).
[10] M.K. Durbin, E.W. Jacobx, J.C. Hicks, and S.-E. Park, Appl. Phys. Lett. **74**, 2848 (1999).