Dry Etching of Germanium Using Inductively Coupled Ar/CCl$_2$F$_2$ /Cl$_2$ Plasma

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In this study, the etch characteristics of Ge are investigated using inductively coupled Ar/CCl$_2$F$_2$/Cl$_2$ plasmas. The etch rate, surface morphology and subtended angle obtained with different etching conditions are presented. The etch rate of Ge increases from 374 Å/min to 520 Å/min as the ICP power increases from 400 to 700 W, whereas the etching rate of Ge decreases from 524 Å/min to 400 Å/min as CCl$_2$F$_2$ flow increases from 40 sccm to 80 sccm. In addition, the etching rate of Ge decreases from 467 Å/min to 400 Å/min as the Cl$_2$ flow increases from 0 sccm to 20 sccm. As the ICP power increases the subtended angle also increases. According to SEM imagery Ar/CCl$_2$F$_2$/Cl$_2$ ICP etching leads to the presence of carbon-based material in the form of large particles.

Keywords: dry etching, plasma, ICP, Germanium

1. INTRODUCTION

Applying of a dry etching technique to Ge and related compounds is one of the key processing steps in fabricating integrated photonic devices and circuits.[1-3] Compared to wet chemical etching, dry etch schemes are more attractive for device manufacturing due to their anisotropic profiles, increased etch uniformity, and reproducibility. For such systems, Ge devices are designed in the micrometer and sub-micrometer ranges where the chemical etchings would have undesirable effects related to the etch controllability and the nature of the sidewall profiles. These undesirable effects can cause degradation of the electrical and optical properties of the device and/or prevent it from functioning as designed. Dry etching of Ge using CF$_4$/HBr/CCl$_2$F$_2$/Cl$_2$ has also been demonstrated to achieve anisotropic profiles at room temperature. Thus, in more common processes such as reactive ion etching (RIE), Electron cyclotron resonance (ECR), and inductively coupled plasma (ICP), chlorine is commonly used to achieve a smooth and anisotropic etching result. Chlorine-based plasmas are widely used for the etching of Si; they enable anisotropic etching owing to the low spontaneous reaction rate of chlorine with silicon and sidewall passivation. Traditionally, chlorine-based plasmas have been used for the dry etching of semiconductor materials,[4-11] as this process makes the patterning of dielectrics on compound semiconductors particularly simple in conjunction with fluorine-containing (CF$_4$, SF$_6$, NF$_3$) plasmas.[12] Typical gases that are used in this process are Cl$_2$, SiCl$_2$, BCl$_3$ or CCl$_2$F$_2$ with additions of argon, helium or oxygen to provide easier ignition of the plasma, more stable operation or dilution to control the etch rate. Pure chlorine tends to have extremely fast etching rates and leaves a rough surface because the native oxides on the semiconductor surface are not removed in a uniform fashion. The gases of Cl$_2$, SiCl$_2$ and BCl$_3$ are all toxic and corrosive and require careful handling. In contrast, CCl$_2$F$_2$ is quite safe and does not need any special safety considerations. Ar is often mixed with chemistries in the dry etching of semiconductors[13,14] for several reasons. It helps to stabilize the plasma discharge, improves activation of the surface by ion bombardment, and increases the dissociation efficiency of chemistries.[15,16] The motivation for adding Ar to the chemistry is to enhance the chemical and physical etching mechanisms. This has been reported by several groups.[17-19] The CCl$_2$F$_2$ plasma chemistry appears promising for the shallow, corrosive-free etching of Ge and Si. It is nonetheless a physically dominated chemistry; hence mask erosion can be prohibitive for deep etching. This chemistry still requires a high-density reactor to produce practical etch rates. By comparison, Cl$_2$-based chemistries produce high rates due to a stronger chemical component; hence, there is less mask erosion. From a technological point of view it is important to understand the possible etch rate ratio of Ge with respect to the Si and photoresist, as well as what types of etch profiles may be produced in Ge.

In this paper, the etch characteristics of Ge were investigated using inductively coupled plasmas in Ar/CCl$_2$F$_2$/Cl$_2$ gas mixtures under varied ICP powers, CCl$_2$F$_2$ flows, and Cl$_2$ flows in an effort to achieve the optimum etching condition.

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2. EXPERIMENTAL PROCEDURE

Samples used for etching experiments were typically, 1×1 cm in size cut from starting two-inch n-type (100) oriented Ge substrates. They were cleaned in a Class 100 clean room using acetone and methanol in an ultrasonic bath for a period of 5 min for each solvent. Thereafter, samples were rinsed under DI water, blow-dried with N_2 gas and pre-baked in an oven at 90°C for 10 min. After heating, they were spin-coated using a spin-coater with photo-resist at 5000 rpm for 30 s and then placed in an oven for soft baking at 90°C for 30 min. Photo-lithography was performed using a mask aligner I-line with ultraviolet light (365 nm) at an intensity of approximately 5 mW. Four-inch mask plates with the features of lines were used for the patterning.

The samples were etched in a load-locked BMR (HiEtch) high-density plasma etch system consisting of an ICP chamber(operating at 2 MHz) and an additional RF bias (13.56 MHz) for the sample chuck. Helium back-side cooling was incorporated to allow the temperature of the substrate to be controlled more effectively. The samples were mounted on a 6 in. Si carrier wafer with vacuum grease before they were introduced into the etching chamber. $Ar/CCl_2F_4 /Cl_2$ gas of 99.999% purity was introduced for etching with varying process parameters. After the etching process, the etch depth in Ge was determined using a á-step surface profiler after the removal of the photo-resist mask. The etch profile and morphology were examined using a scanning electron microscope (SEM).

3. RESULT AND DISCUSSION

The effects of the etching Ge material after varying the processing parameters of the ICP power, CCl_2F_2 flow and Cl_2 flow are discussed in this section. First, the etch rates and sidewall profiles were determined as a function of the ICP power. Samples were etched for 3 min at constant parameters an Ar flow of 20 sccm, a CCl_2F_2 flow of 40 sccm, a Cl_2 flow of 10 sccm, a bias power of 100 W, a pressure of 5 mTorr and a temperature of 20°C. Figure 1 shows the results of the etch rates for Ge as a function of the ICP power. As shown in the figure, the etch rate of Ge increases from 374 Å/min to 520 Å/min as the ICP power increases from 400 W to 600 W. This is due to the higher concentration of reactive species, which increases the chemical component in the etching mechanism. As a result of the higher ion flux, there is an increase in the bond breaking and sputter adsorption of the etching mechanism.[20] SEM images of Ge samples etched at ICP power of 300 W and 500 W are shown in Fig. 2. This image shows the edge profile to be a gradual slope, indicating good anisotropy. Moreover, the etched surface appears smooth, indicating that little surface damage has occurred. This figure clearly shows that the subtended angle increases
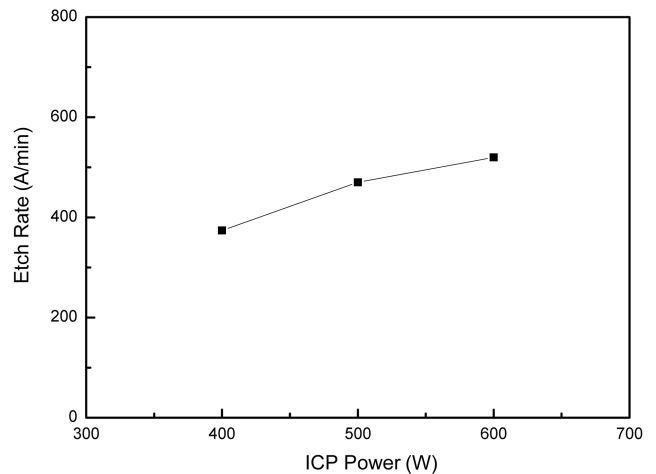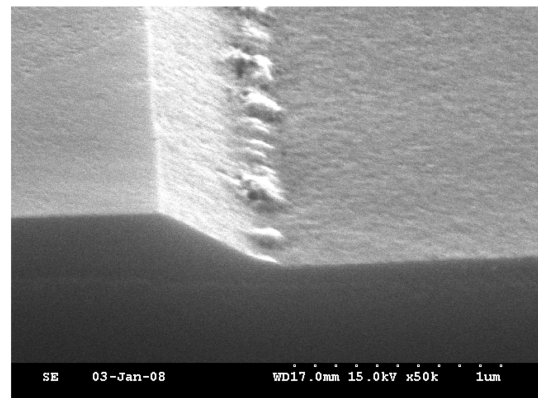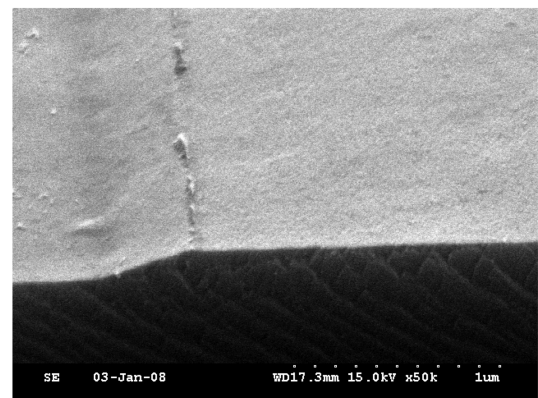

Fig. 1. Etch rate of Ge as a function of the ICP Power.

(a)

(b)

Fig. 2. SEM images of Ge sample etched at ICP power of (a) 300 W and (b) 500 W.

as the ICP power increases. The reason for the increase in the angle with the increase in the ICP power is most likely due to the amount of $GeCl_4$ and GeF_4 that form in the smooth of sidewalls as a result of the ICP power.[15]

Second, the etch rates and sidewall profiles were deter-

mined as a function of the CCl_2F_2 flow. The samples were etched for 3 min at constant parameters of an Ar flow of 20 sccm, a Cl_2 flow of 10 sccm, a bias power of 100 W, an ICP power of 400 W, a pressure of 5 mTorr, and a temperature of 20°C. Figure 3 shows the results of the etch rates for Ge samples as a function of the CCl_2F_2 flow. This figure shows that the etch rate of Ge decreases from 524 Å/min to 400 Å/min as the CCl_2F_2 flow increases from 40 sccm to 80 sccm. Additionally, the etch rate of Si decreases from 2400 Å/min to 1396 Å/min as the CCl_2F_4 flow increases from 40 sccm to 80 sccm. Increasing the CCl_2F_4 flow increases the density of the reactive species present in the chamber. However, it also decreases the mean free path, thereby affecting the energy with which the ions impinge on the substrate and the average lifetime of the ions before they recombine. This occurs because the mean free path of ions can be reduced and thus become much shorter than the length of the sheath in the plasma at a high CCl_2F_4 flow. This effect can reduce the directionality of the ions impinging on the Ge samples, thereby reducing the etch rates at a higher CCl_2F_4 flow. Although the chemistry of these discharges is highly complex, it is likely that the surface chemistry effects play a dominant role in these systems, as the surfaces of the Ge are greatly modified by the deposition of chlorine, fluorine and carbonaceous materials. For CCl_2F_2 plasmas, the deposition of chlorine is reduced but deposition of carbonaceous material takes place simultaneously.[20] The chlorine-, fluorine- and carbon-based over-layers are sufficiently thick (greater than several monolayer) and therefore affect the etching of the Ge. The SEM images show that for $Ar/CCl_2F_2/Cl_2$ ICP etching causes the presence of the chlorine-, fluorine- and carbon-based material in the form of large particles. These large particles are ineffective in blocking a fluorine attack on the germanium substrate. The particulates can be formed in etching plasmas via negative ions localized at the sheath boundary just above the surface of the wafer.[15] These parti-
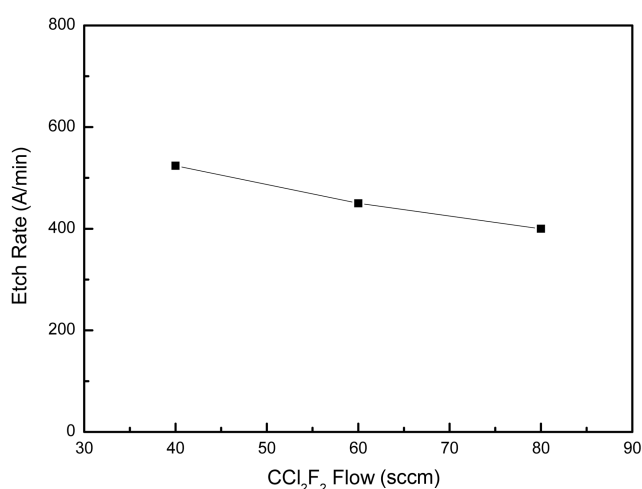
cles remain in a negative charge state for a long time and grow in size while floating above the wafer surface. Eventually, they are neutralized and become deposited onto the wafer. SEM images of Ge sample etched at a CCl_2F_2 flow of 40 sccm and 80 sccm are shown in Fig. 4. In the figure, The Ge sample shows that the etched sidewalls are rough at an angle of approximately 65° at a CCl_2F_2 flow of 80 sccm. The Ge surface has a very grainy appearance due to the deposition of carbon-related materials. Chlorine and fluorine may therefore have been constituents of these particles after ICP etching.[9] Although rough surfaces are often observed after etching, the shape of the particles in Fig. 4 is different from what is typically observed on a surface formed by micromasking. The common constituent of most of etching chemistries of a mixture is chlorine, which is attractive because germanium chlorides are volatile at relatively low temperatures, as opposed to stable germanium fluorides. Most of Cl-containing gases also contain carbon, and often carbon and other problematic materials are encountered with the deposition of polymeric films on a Ge surface during etching. This figure also shows that subtended angle also increases as the CCl_2F_2 flow increases. The largest angles observed are approximately 60° and 75° at CCl_2F_2 flows of 40 sccm and
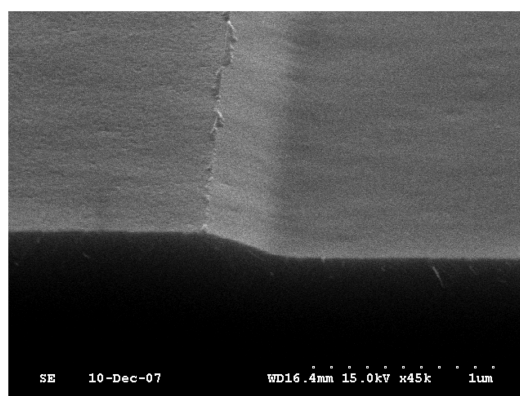
(a)
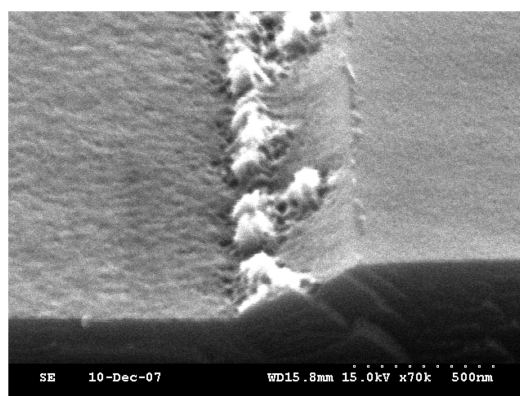
(b)

Fig. 4. SEM image of Ge sample etched at a CCl_2F_2 flow of (a) 40 sccm and (b) 80 sccm.

Fig. 3. Etch rate of Ge as a function of the CCl_2F_2 flow.

80 sccm, respectively. The cause of the increase in the angle with the increase in the CCl_2F_2 flow is most likely the amounts of $GeCl_4$ and GeF_4 that form in the flaring of the sidewalls as a result of the CCl_2F_2 flow.[21]

Third, the etch rates and sidewall profiles were determined as a function of the Cl_2 flow. Samples were etched for 3 min at constant parameters of an Ar flow of 20 sccm, a CCl_2F_2 flow of 40 sccm, a bias power of 100 W, an ICP power of 400 W, a pressure of 5 mTorr and a temperature of 20°C. The results of the etch rates for Ge as a function of the Cl_2 flow are shown in Fig. 5. This figure illustrates that the etching rate of Ge decreases from 467 Å/min to 400 Å/min as the Cl_2 flow increases from 0 sccm to 20 sccm.[9] Increasing the Cl_2 flow increases the density of the reactive species present in the chamber. However, it also decreases the mean free path, thereby affecting the energy with which the ions impinge on the substrate as well as the average lifetime of the ions before they recombine. This transpires because the mean free path of the ions can be reduced until they are much shorter than the length of the sheath in the plasma at a high Cl_2 flow. This effect can reduce the directionality of the ions impinging on the Ge samples, thereby reducing the etch rates at higher Cl_2 flows. Moreover, SEM images of a sidewall profile of a Ge sample etched using $Ar/CCl_2F_2/Cl_2$ chemistry at Cl_2 flows of 10 sccm and 30 sccm are shown as a comparison in Fig. 6. This figure shows that the Cl_2 flow increases while the subtended angle decreases. The figure also shows that the etched sidewalls of the Ge sample are smooth at an angle of approximately 65° at a Cl_2 flow of 10 sccm. However the etched profile of the Ge at a Cl_2 flow of 30 sccm has highly vertical walls. The CCl_2F_2 plasma chemistry appears to be promising for shallow, corrosive-free etching of Ge. It remains a physically dominated chemistry; implying that mask erosion can be prohibitive for deep etching. This chemistry continues to require a high density reactor to produce practical etch rates. In comparison, Cl_2-based chemistries produce high rates due to a stronger chemical component; hence, there is less mask erosion. The etch mechanism involves a reaction of a thin chlorinated surface layer, which is removed by ion-assistance before it can build into a nonvolatile selvedge region. The key difference that occurs with high-density conditions is that high ion flux balances the formation and removal of the chlorinated etch product layer. For Cl_2-based chemistries, the mass of the additive (Ar) has a considerable impact on the Ge etch rate. Moreover, the same basic trends are observed with an addition of Ar. As Cl_2 is added to the discharge, the etch rates initially increase as the chemical component is introduced. However, beyond particular Cl_2 compositions the etch rates decrease again because the ion-to-neutral ratio becomes too low, allowing a chlorinated selvedge layer to form on the surface. Due to the higher Ge etch rates associated with Cl_2 as compared to CCl_2F_2, the feature anisotropy was better in the former trial because less mask erosion occurred. Severe corrosion was observed on Cl_2-etched samples unless post-etch cleaning was performed immediately after the removal of the samples from the reactor. The common constituent of most of etching chemistries of a mixture is chlorine, which is attractive because germanium chlorides are volatile at rela-
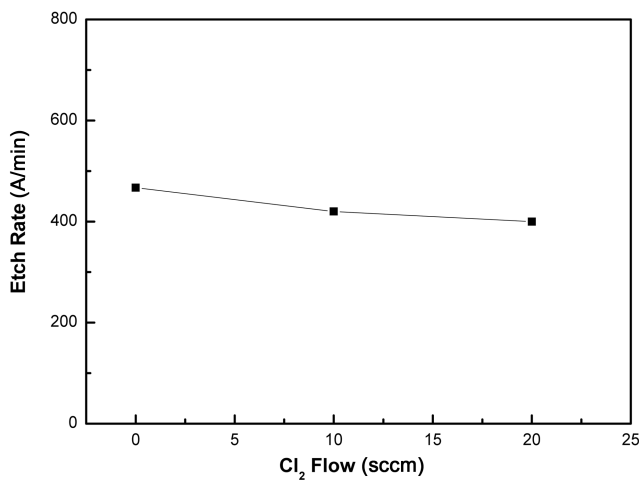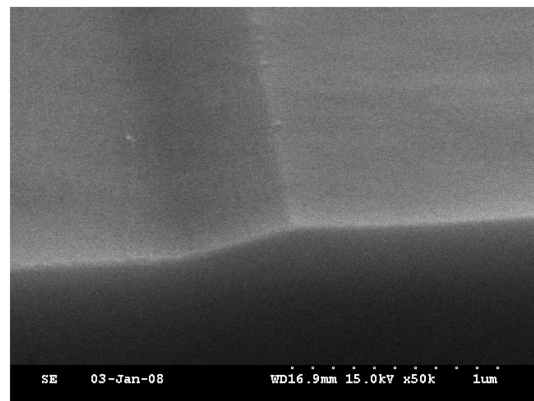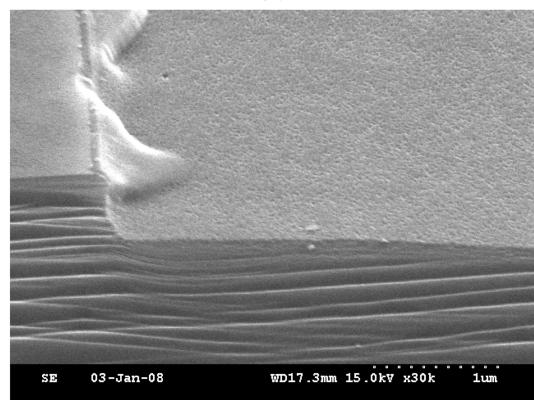
(a)

(b)

Fig. 6. SEM image of Ge sample etched at the Cl_2 flow of (a) 10 sccm and (b) 30 sccm.

Fig. 5. Etch rate of Ge as a function of the Cl_2 flow.

tively low temperatures as opposed to the stable germanium fluorides. Most of Cl-containing gases also contain carbon, and often carbon and other problems are encountered during the deposition of polymeric films on the surface of Ge during etching, as mentioned above, leading to irreproducible results.

4. CONCLUSION

A systematic study of ICP etching on Ge (100) samples with Ar/CCl$_2$F$_2$/Cl$_2$ chemistry was conducted by varied several processing parameters. The etch rate of Ge increases from 374 Å/min to 520 Å/min as the ICP power increases from 400 W to 700 W. However the etching rate of the Ge material decreases from 524 Å/min to 400 Å/min as the CCl$_2$F$_2$ flow increases from 40 sccm to 80 sccm. Moreover, the etching rate of Ge decreases from 467 Å/min to 400 Å/ min as the Cl$_2$ flow increases from 0 sccm to 20 sccm. As the ICP power is increases, the subtended angle also increases. SEM images demonstrate that the Ar/CCl$_2$F$_2$/Cl$_2$ ICP etching leads to the presence of carbon-based materials in the form of large particles. Consequently, the optimum etching condition of Ge using inductively coupled Ar/CCl$_2$F$_2$/Cl$_2$ plasmas was successfully determined as follows: an ICP power of 400 W, a CCl$_2$F$_2$ flow of 60 sccm, a Cl$_2$ flow of 10 sccm, a bias power of 100 W, an ICP power of 400 W, a pressure of 10 mTorr, and a temperature of 20°C.

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REFERENCES

1. U. Gnutzmann and K. Clausecker, *Appl. Phys.* **3**, 9 (1974).
2. E. Kasper, H. Kibbel, H.-J. Herzog, and A. Gruhle, *Jpn. J. Appl. Phys.* **33**, 2415 (1994).
3. T. S. Kim, S.-S. Choi, T. S. Jeong, S. Kang, C-J. Choi, and K-H. Shim, *Electron. Mater. Lett.* **5**, 95 (2009).
4. T. S. Kim, H. Y. Yang, Y. -H. Kil, S. S. Choi, T. S. Jeong, S. Kang, and K. H. Shim, *J. Korean Phys. Soc.* **55**, 1799 (2009).
5. M. Rahman, N. P. Johnson, M. A. Foad, A. R. Long, M. C. Holland, and C. D. W. Wilkinson, *Appl. Phys. Lett.* **61**, 2335 (1992).
6. T. S. Kim, H. Y. Yang, S. S. Choi, T. S. Jeong, S. Kang, and K. H. Shim, *J. Korean Phys. Soc.* **56**, 59 (2010).
7. R.A. Barker, T. M. Mayer, and R. H. Burton, *Appl. Phys. Lett.* **40**, 583 (1982).
8. V. M, Donnelly, D. L. Flamm, C. W. Tu, and D. E. Ibbottson, *J. Electrochem. Soe.* **129**, 2533 (1982).
9. K. B. Jung, H. Cho, Y. B. Hahn, E. S. Lambers, S. Onishi, D. Johnson, A. T. Hurst, Jr., J. R. Childress, Y. D. Park, and S. J. Pearton, *J. Appl. Phys.* **85**, 4788(1999)
10. T. S. Kim, H. Y. Yang, S.-S. Choi, T. S. Jeong, S. Kang, and K-H. Shim, *Electron. Mater. Lett.* **5**, 43 (2009).
11. S. J. Pearton, U. K. Chakrabarti, W. S. Hobson, and A. Perley, *J. Electrochem. Soc.* **137**, 3188 (1990).
12. T. S. Kim, H. Y. Yang, Y. H. Kil, T. S. Jeong, S. Kang and K. H. Shim, *J. Korean Phys. Soc.* **54**, 2290 (2009).
13. L. Henry, C. Vaudry, A. le Corre, D. Lecrosnier, P. Alnot, and J. Olivier, *Electron. Lett.* **23**, 1254 (1987).
14. S. J. Pearton, U. K. Chakrabarti, A. P. Perley, C. Constantine, and D. Johnson, *Semicond. Sci. Technol.* **6**, 929 (1991).
15. S. J. Pearton and F. Ren, *J. Mater. Sci.* **5**, 1 (1994).
16. V. J. Law, M. Tewordt, S. G. Ingram, and G. A. C. Jones, *J. Vac. Sci. Technol. B* **9**, 1149 (1991).
17. S. J. Pearton, U. K. Chakrabarti, E. Lane, A. P. Perley, C. R. Abernathy, and W. S. Hobson, *J. Electrochem. Soc.* **139**, 856 (1992).
18. A. T. Ping, I. Adesida, M. Khan, and J. N. Kuznia, *Electron. Lett.* **22**, 1895 (1994).
19. V. J. Law, M. Tewordt, S. G. Ingram, and G. A. C. Jones, *J. Vac. Sci. Technol. B* **9**, 1149 (1991).
20. L. Stafford, J. Margot, S. Delprat, M. Chaker, and S. J. Pearton, *J. Appl. Phys.* **101**, 083303 (2007)
21. G. S. Oehrlein, T. D. Bestwick, P. L. Jones, M. A. Jaso, and J. L. LindstrSrn, *J. Electrochem. Soc.* **138**, 1443 (1991).