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Si in GaN – ON THE NATURE OF THE BACKGROUND DONOR

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Abstract

A characterization of the Si impurity in GaN is performed by Raman spectroscopy. Applying hydrostatic pressure up to 25 GPa we study the behavior of the LO phonon-plasmon mode in a series of high mobility Si doped GaN films. In contrast to earlier results on unintentionally doped bulk GaN crystals no freeze out of the free carriers could be observed in Si doped samples. We find that Si is a shallow hydrogenic donor throughout the pressure range studied. This result positively excludes Si incorporation as a dominant source of free electrons in previously studied bulk GaN samples.

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gallium nitride, donor, Raman, hydrostatic pressure

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Considerable progress in the growth of wide bandgap nitrides, especially GaN [1], has led to high performance optoelectronic devices [2]. Despite the spectacular progress it is still widely recognized that optical [3] and electrical [4] properties of GaN are significantly affected by unintentionally introduced defects and/or impurities.

A problem common to very different growth techniques of GaN, such as metal organic vapor phase epitaxy, molecular beam epitaxy and different kinds of vapor phase techniques is a high n-type carrier concentration for some choices of thermodynamic parameters. A good example are small bulk single crystals of as grown GaN which have a free carrier concentration of 10^{19} – 10^{20} cm^{-3} [5]. Although, so far, the origin of the residual donors has not been positively identified it has been shown that under large enough hydrostatic pressure the electrons freeze out onto localized states in the band gap [6–8]. These results were interpreted in terms of a highly localized donor defect emerging from the conduction band at large pressures. A native defect is expected to show such a behavior, however, a pressure induced transformation of the groundstate of a hydrogenic defect could not be excluded [7]. Such a transformation into a strongly localized DX-like configuration is a commonly observed feature in other compound semiconductors [9]. In order to distinguish between those two possible interpretations we have performed a Raman study of the phonon-plasmon coupling in intentionally Si doped GaN under large hydrostatic pressure.

High quality films of GaN at a typical thickness of $3\,\mu m$ were grown by metal organic vapor phase epitaxy on (0001) sapphire. In an established and stable process low background n-type conductivity can be achieved and the free electron concentration can be controlled by doping of Si. Here we present results on samples with room temperature free electron concentrations of $N = 8.6 \times 10^{16}$, 3×10^{18} and $1 \times 10^{19}\,cm^{-3}$ and Hall mobilities of 412, 232, $171\,cm^2/Vs$, respectively. From the wide range of controllably obtained electron densities we conclude that more than 99 % of the active donors in the highly doped samples are due to Si. Non resonant Raman spectroscopy was performed using 120 mW of the 476.5 nm line of an Ar ion laser. Absolute phonon energies are given at an accuracy of $\pm 1\,cm^{-1}$. Samples were thinned to about $25\,\mu m$ thickness by polishing of the substrate. The final sample

diameter was about 200 μm. Hydrostatic pressure was applied by means of a Mao-Bell type diamond anvil cell using a methanol/ethanol (4:1) mixture as a pressure medium. Pressure was monitored by standard ruby fluorescence and subsequently by the E_2 phonon mode of GaN as a secondary standard. All data were taken at room temperature.

Raman data in $z(x,-)\bar{z}$ back scattering geometry of the sample series is shown in Fig. 1. From inspection of the Raman tensor [11] we realize that A_1(LO) and E_2 are allowed in this geometry. In the thin GaN film with the lowest electron concentration (8.6×10^{16} cm^{-3}) these modes are identified at: E_2(high) at 566.7 cm^{-1} and A_1(LO) 739.5 cm^{-1}. These values are very close to data obtained on thick films from high temperature vapor phase epitaxy [12] E_2(high) 566.4 cm^{-1}, and the A_1(LO) at 738.8 cm^{-1}. At a thickness of about 20 μm these values represent bulk data at a carrier concentration of $\approx 10^{17}$ cm^{-3}. The small variation is due to biaxial stress components in the thin films grown on lattice mismatching sapphire [13]. At higher electron concentration (3×10^{18} and 1×10^{19} cm^{-3}) the A_1(LO) mode is not observable. The mode at 755 cm^{-1} is sapphire related and it disappears in a thinned sample. The optical GaN mode couples to the electron plasma [14] and as an over damped mode vanishes in the background signal for higher electron concentration. As has been shown in the literature presence, the position and line shape of the coupled mode are a very sensitive measure of the free electron concentration in the range of 10^{17} to 10^{18} cm^{-3} [15,7]. In a curve fitting procedure to the A_1(LO) mode we use the parameters of Ref. [15] and a scattering rate determined from the Hall mobility. For the low doped sample we determine a free electron concentration of 9.1×10^{16} cm^{-3} in very good agreement with the Hall data (dotted line in Fig. 1). Using the respective parameters for the higher doped samples we find that their coupled modes should appear as very broad and weak signals only (dotted lines) and would vanish in the background. As seen from these results this method provides a convenient way to optically monitor transport properties. This is especially helpful in a study of the hydrostatic pressure dependence of a sample within a diamond anvil cell.

Data on the low doped ($N = 8.6 \times 10^{16}$ cm^{-3}) sample obtained in $z(x,-)z$ forward scattering as a function of applied hydrostatic pressure is shown in Fig. 2 (normalized to the

peak height of the E_2 mode). Both E_2 and A_1(LO) modes are well resolved in the pressure range up to 16 GPa. For this 3 μm film of GaN on (0001) sapphire we find a linear increase of the E_2 mode with pressure of

$$E_2(\text{high}): \qquad \nu = 566.7\,\text{cm}^{-1} + 3.75\,\text{cm}^{-1} \times p/\text{GPa}\,. \tag{1}$$

A similar linear increase is found for the A_1(LO) mode:

$$A_1(LO): \qquad \nu = 739.2\,\text{cm}^{-1} + 3.53\,\text{cm}^{-1} \times p/\text{GPa}\,. \tag{2}$$

The relative pressure coefficient $d\nu_{A1LO}/dp : d\nu_{E2}/dp = 0.94$ is pressure independent and varies by ± 0.02 in our data. The intensity ratio of the two modes is very little affected by the pressure. We always find the A_1(LO) mode at 5 – 10 % of the peak height of E_2. Unlike the LO mode, E_2 is not affected by the electronic susceptibility and can be used as an internal reference for the scattering intensity.

On the background of this information we know where to expect the coupled mode in the highly doped sample once the carrier concentration drops below $10^{18}\,\text{cm}^{-3}$. Fig. 3 gives the data for $N = 1 \times 10^{19}\,\text{cm}^{-3}$ in a wide pressure range up to 25 GPa. At the highest pressure the A_1(LO) mode should be expected at $827\,\text{cm}^{-1}$ (Eq. 2). As seen from the results at ambient pressure and in the case of the bulk material [7,6] a well resolvable signal at an intensity of 5 – 10 % of the E_2 mode can be expected for an A_1(LO) mode decoupled from the plasma.

Fig. 4 collects the large pressure data obtained for the several samples. For the lightly ($8.6 \times 10^{16}\,\text{cm}^{-3}$) Si doped sample the A_1(LO) mode is visible at $827\,\text{cm}^{-1}$ but there is no indication for the presence of the peak in the highly Si doped ($1 \times 10^{19}\,\text{cm}^{-3}$) one. At the given signal-to-noise level a decoupled or even weakly coupled mode at a carrier concentration below $10^{18}\,\text{cm}^{-3}$ would have been observable. For comparison the spectrum obtained on the $1 \times 10^{19}\,\text{cm}^{-3}$ bulk crystal at 27 GPa [7] clearly exhibits this mode at $825\,\text{cm}^{-1}$ (Fig. 4).

We conclude that the free carrier concentration in Si doped GaN films can not be reduced from 1×10^{19} to below $10^{18}\,\text{cm}^{-3}$ by application of hydrostatic pressure up to 25 GPa at

room temperature. This is in striking contrast to highly n-type unintentionally doped bulk GaN. There an appearance of the LO phonon and a significant reduction of the free carrier concentration was observed at 20, 25 and 27 GPa. At the highest pressure a remaining concentration of $3 \times 10^{17}\,\mathrm{cm}^{-3}$ was determined [7]. From the knowledge of the electron density we derived a localization energy of about 126 meV with respect to the conduction band edge at 27 GPa.

In the present experiment we find that application of pressure up to 25 GPa does not significantly increase the binding energy of the Si donor. Under ambient conditions its binding energy of about 27 meV [16] is close to the effective mass value of 35.5 meV [17]. From this experimental evidence we conclude that Si is an effective mass type donor in GaN which does not undergo a transformation to a DX-like configuration at hydrostatic pressures up to 25 GPa. This finding is in agreement with recent theoretical predictions [18]. From the analogy of application of hydrostatic pressure to GaN with an alloying with Al we expect Si to be a hydrogenic donor in $Al_xGa_{1-x}N$ for $x < 0.7$ as well.

In summary we performed a study of the pressure dependence of the electron phonon interaction in Si doped GaN. In contrast to highly n-type bulk crystals no pressure induced freeze out of electrons could be observed for $p \leq 25$ GPa. We conclude that Si behaves like a hydrogenic donor in the whole pressure range and therefore Si cannot be responsible for the high n-type conduction of unintentionally doped bulk GaN crystals. We

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REFERENCES

[a] Current address: Lam Research, 4650 Cushing Parkway, Fremont, CA 94538, USA.

[1] I. Akasaki and H. Amano, J. Crystal Growth **146**, 455 (1995).

[2] S. Nakamura, M. Senoh, S.-I. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, Jpn. J. Appl. Phys. 2, Lett. **35**, L74 (1996).

[3] C. Wetzel, D. Volm, B.K. Meyer, K. Pressel, S. Nilsson, E.N. Mokhov, and P.G. Baranov, Appl. Phys. Lett., **65**, 1033 (1994).

[4] R.J. Molnar, T. Lei, and T.D. Moustakas, Appl. Phys. Lett., **62**, 72 (1993).

[5] H. Teisseyre, P. Perlin, M. Leszczynski, T. Suski, I. Grzegory, J. Jun, S. Porowski, and T.D. Moustakas, J. Appl. Phys. **76**, 2429 (1994).

[6] P. Perlin, T. Suski, H. Teisseyre, M. Leszczynski, I. Grzegory, J. Jun, S. Porowski, P. Boguslawski, J. Bernholc, J.C. Chervin, A. Polian, and T.D. Moustakas, Phys. Rev. Lett., **75**, 296 (1995).

[7] C. Wetzel, W. Walukiewicz, E.E. Haller, J.W. Ager III, I. Grzegory, S. Porowski, and T. Suski, Phys. Rev. B, **53**, 1322 (1996).

[8] see also P. Perlin, W. Knap, J. Camassel, A. Polian, J.C. Chervin, T. Suski, I. Grzegory, and S. Porowski, Seventh Int. Conf. High Pressure Semiconductor Physics (July 28-31, 1996, Schwäbisch-Gmünd, Germany).

[9] M. Mizuta, M. Tachikawa, H. Kukimoto, and S. Minomura, Jpn. J. Appl. Phys. **24**, L143 (1985).

[10] see e.g. J. Neugebauer and C.G. Van de Walle, 22nd Int. Conf. Physics Semicond., Vancouver 1994 (World Scientific Publishing Co, Singapore) p. 2327.

[11] C. A. Arguello, D. L. Rousseau, and S. P. S. Porto, Phys. Rev. **181**, 1351 (1969).

[12] S. Fischer, C. Wetzel, E.E. Haller, and B.K. Meyer, Appl. Phys. Lett. **67**, 1298 (1995). C. Wetzel, S. Fischer, and E.E. Haller, *unpublished.*

[13] C. Wetzel, E.E. Haller, H. Amano, and I. Akasaki, Appl. Phys. Lett. **68**, 2547 (1996).

[14] A. Mooradian, Phys. Rev. Lett. **20**, 1102 (1968).

[15] T. Kozawa, T. Kachi, H. Kano, Y. Taga, M. Hashimoto, N. Koide, and K. Manabe, J. Appl. Phys. **75**, 1098 (1994).

[16] N. Kaneda, T. Detchprohm, K. Hiramatsu, and N. Sawaki, Japn. J. Appl. Phys. 2, **35** L468 (1996).

[17] B.K. Meyer, D. Volm, A. Graber, H.C. Alt, T. Detchprohm, K. Amano, and I. Akasaki, Sol. Stat. Comm. **95**, 597 (1995).

[18] J. Bernholc, P. Boguslawski, E.L. Briggs, B. Chen, K. Rapcewicz, B. Yakobson, and Z. Zhang, in *III-Nitride, SiC and Diamond Materials for Electronic Devices*, eds. D.K. Gaskill, C. Brandt, and R.J. Nemanich, MRS Symposia Proceedings, **423**, (Mat. Res. Soc., Pittsburgh, *unpublished*).

FIGURES

FIG. 1. Raman spectra of Si doped GaN/sapphire films with different electron concentrations. The $A_1(LO)$ mode is observed only in the lowest doped sample. For higher concentration the over damped phonon plasmon coupled mode vanishes in the background signal. The dashed lines correspond to the calculated lineshape [15] using a Faust-Henry coefficient $C = -5.2$.

FIG. 2. Raman spectra of MOCVD-grown GaN in forward scattering geometry under hydrostatic pressure. In the low doped sample E_2 and $A_1(LO)$ mode shift with similar pressure coefficient (T=300 K). The spectra are normalized to the height of the E_2 peak and offset for clarity.

FIG. 3. Raman spectra of a highly Si doped sample over a wide range of hydrostatic pressure values. The spectra are normalized to the heigth of the E_2 mode. The $A_1(LO)$ mode does not appear in its expected range of 730 – 830 cm^{-1}. Note the disappearance of the sapphire related mode in the spectra of the thinned samples in the pressure cell.

FIG. 4. Comparison of the Raman spectra of the two extreme Si doped samples and the unintenionally doped bulk crystal at large pressure. At a comparable signal-to-noise ratio decoupled $A_1(LO)$ modes are observed in the $8.6 \times 10^{16}\,cm^{-3}$ Si doped sample and the $N = 1 \times 10^{19}\,cm^{-3}$ bulk crystal, but no mode is found for the $1 \times 10^{19}\,cm^{-3}$ highly Si doped one.

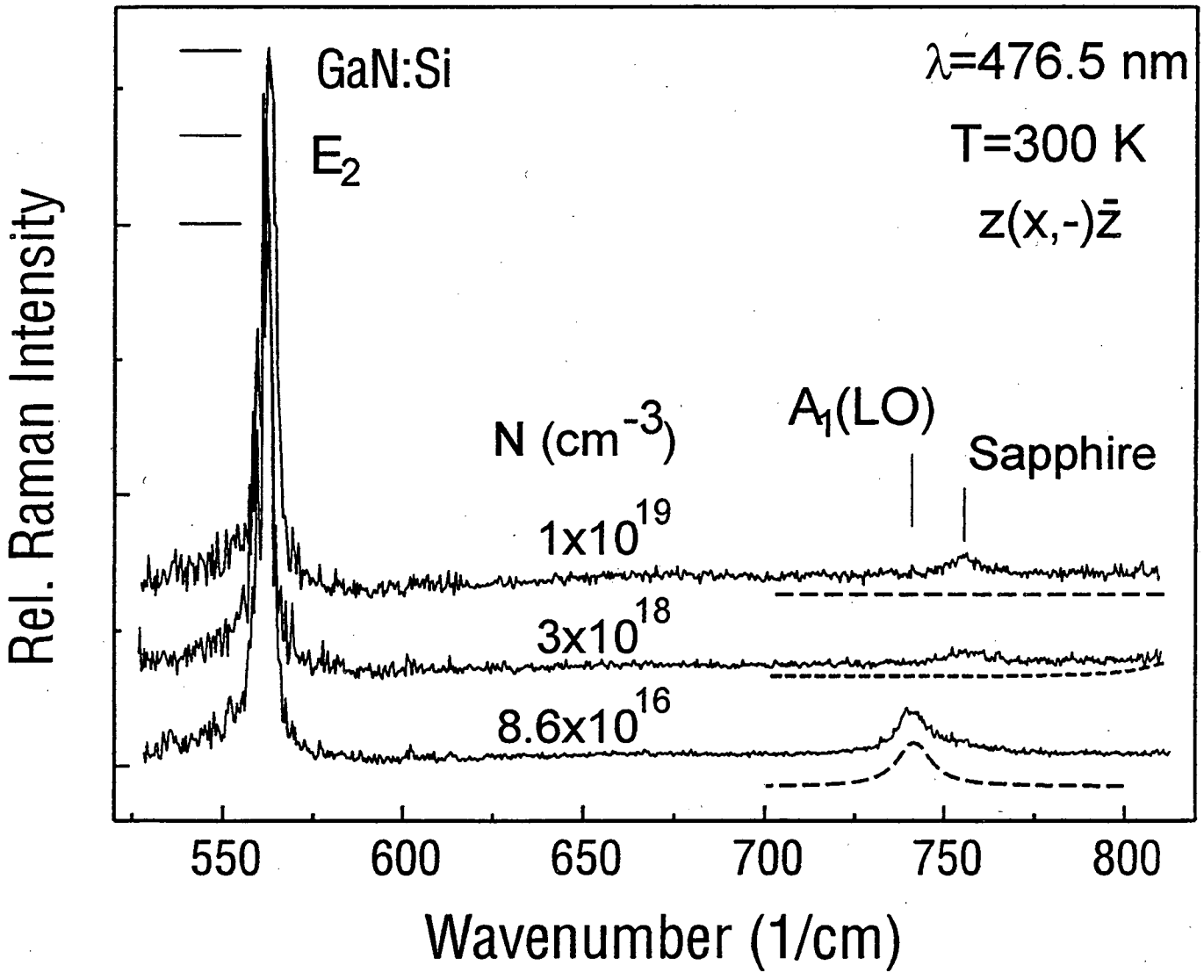

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FIG. 1

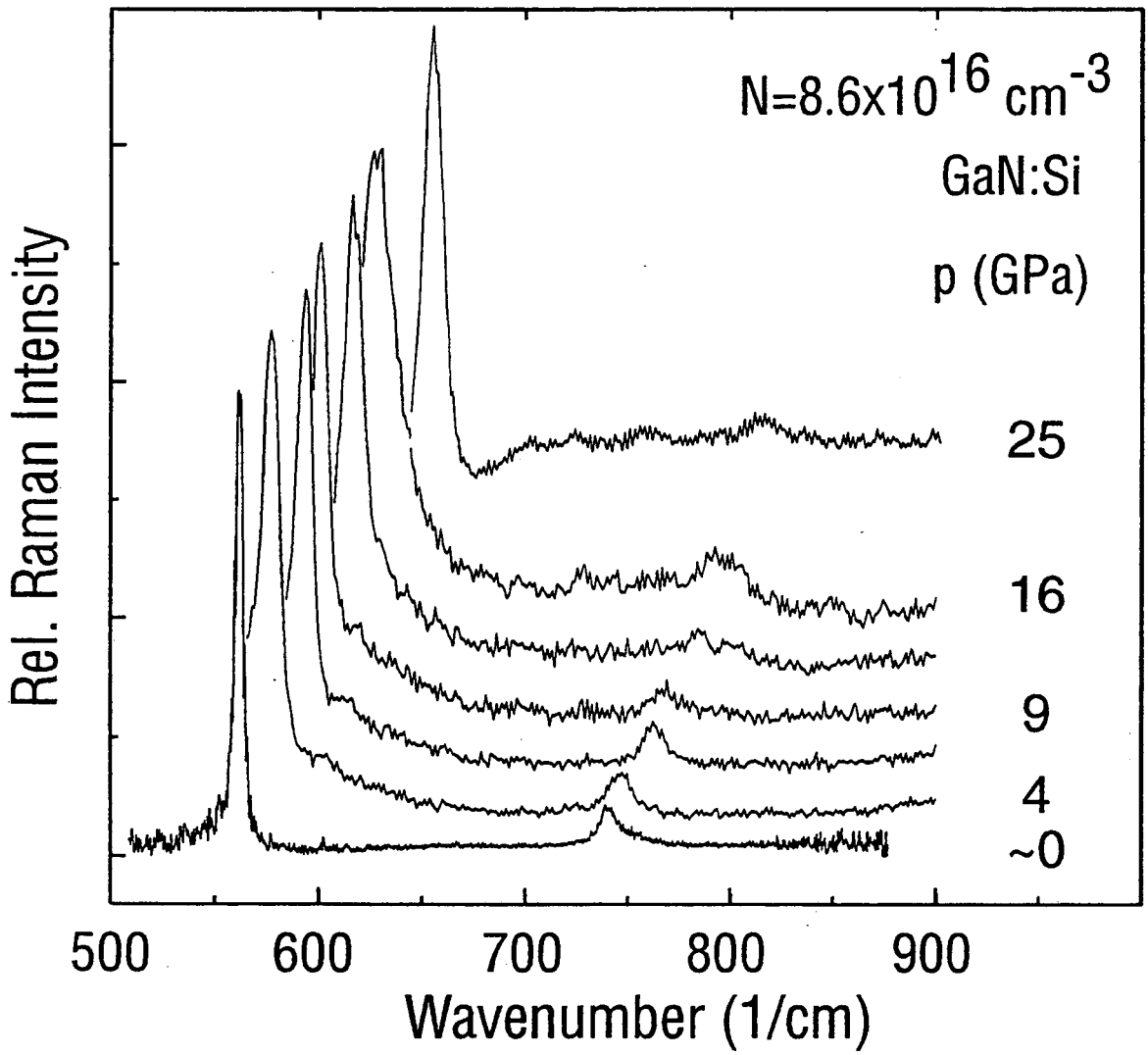

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FIG. 2

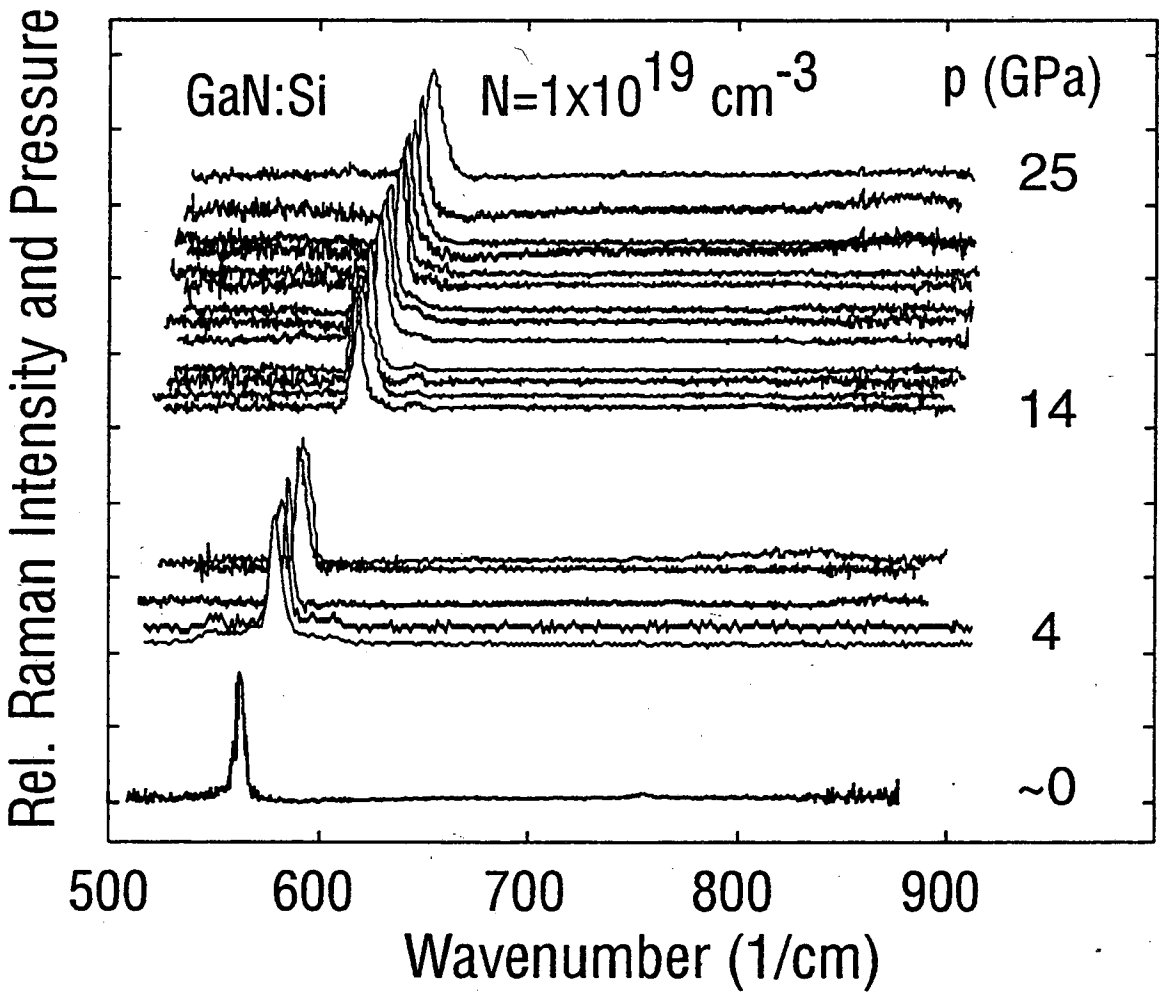

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FIG. 3

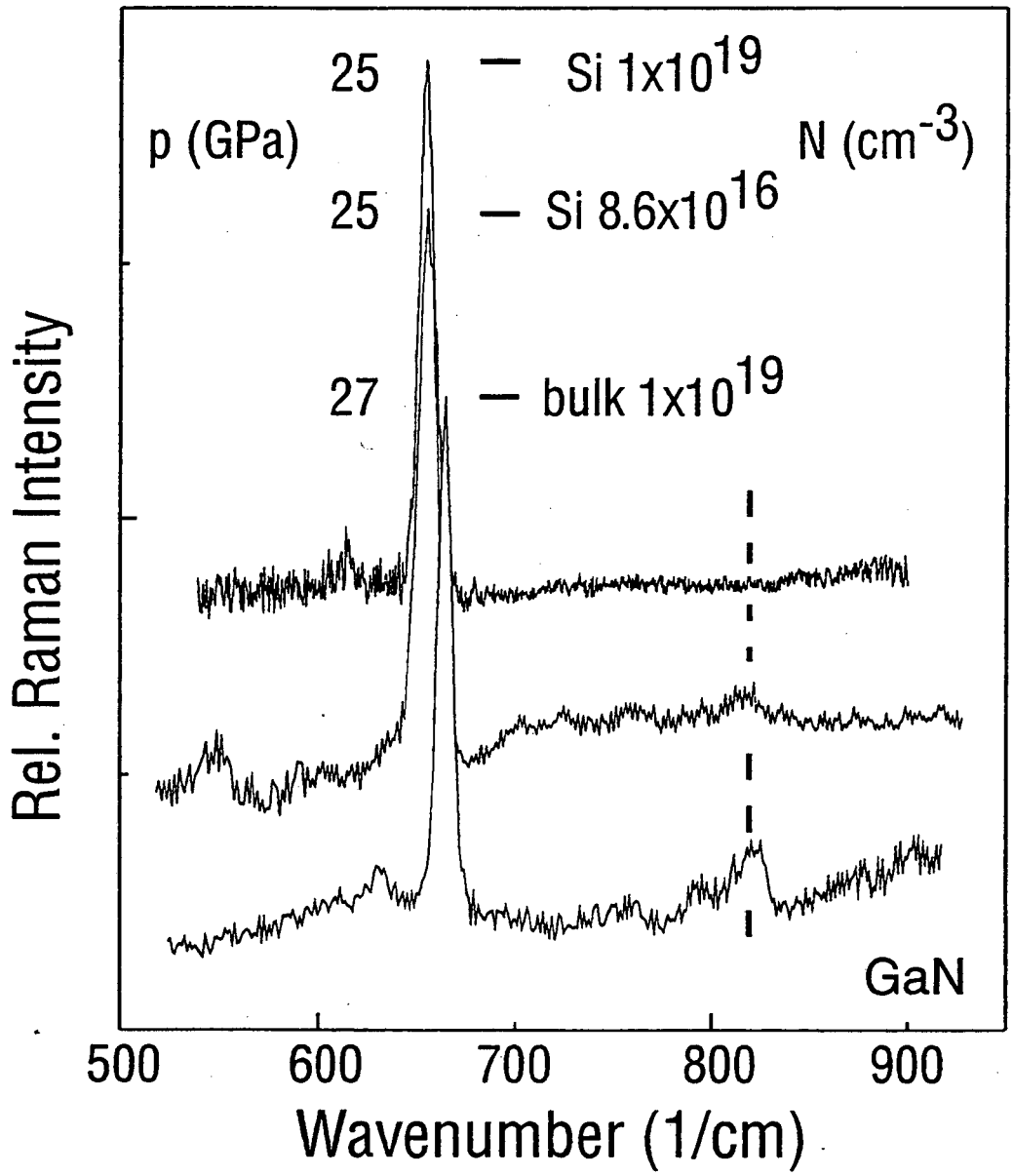

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FIG. 4

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