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Citation: *Applied Physics Letters* **76**, 2889 (2000); doi: 10.1063/1.126507

View online: <http://dx.doi.org/10.1063/1.126507>

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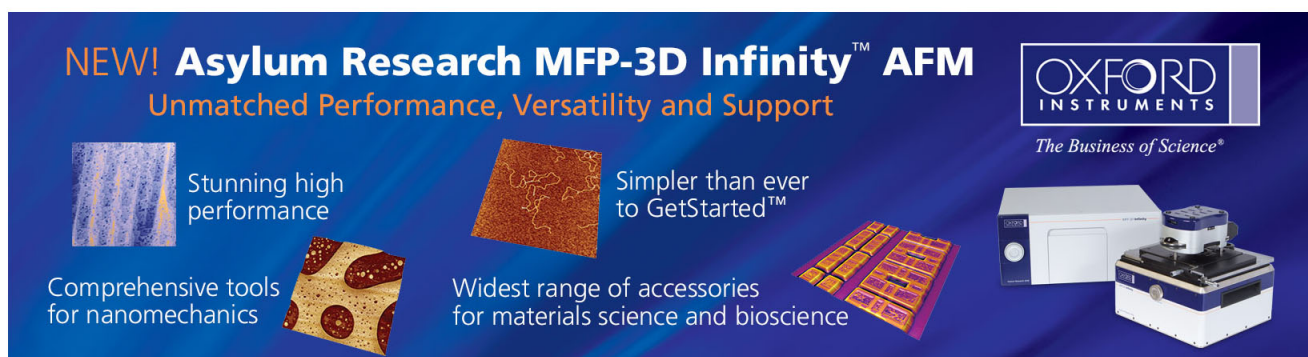
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Observation of electronic Raman scattering from Mg-doped wurtzite GaN

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(Received 6 December 1999; accepted for publication 17 March 2000)

Electronic Raman scattering experiments have been carried out on both molecular beam epitaxy and metal-organic chemical vapor deposition-grown Mg-doped wurtzite GaN samples. Aside from the expected Raman lines, a broad structure (full width at half maximum $\cong 15 \text{ cm}^{-1}$) observed at around 841 cm^{-1} is attributed to the electronic Raman scattering from neutral Mg impurities in Mg-doped GaN. Our experimental results demonstrate that the energy between the ground and first excited states of Mg impurities in wurtzite GaN is about one-half of its binding energy. © 2000 American Institute of Physics. [S0003-6951(00)01420-0]

The recent surge of activity in wide band gap semiconductors¹ has arisen from the need for electronic devices capable of operation at high power levels, high temperatures, and caustic environments, and separately, from a need for optical materials, especially emitters, which are active in the blue and ultraviolet wavelengths. Electronics based upon the existing semiconductor device technologies of Si and GaAs cannot tolerate greatly elevated temperatures or chemically hostile environments. The wide band gap semiconductors with their excellent thermal conductivities, large breakdown fields, and resistance to chemical corrosion will be the materials of choice for these applications. Among the wide band gap semiconductors, the III-V nitrides have long been viewed as a very promising semiconductor system for device applications in the blue and ultraviolet wavelengths. The wurtzite polytypes of GaN, AlN, and InN form a continuous alloy system whose direct band gaps range from 1.9 eV for InN, to 3.4 eV for GaN, and to 6.2 eV for AlN. Thus III-V nitrides could potentially be fabricated into optical devices which are active at wavelengths ranging from the red all the way into the ultraviolet. Because the lower ohmic contact resistances and larger predicted electron saturation velocity² the research of GaN is of particular interest.

P-type doping in nitride-based wide band gap semiconductors has been a big challenge to researchers. The recently successful *p*-type doping in metal-organic vapor phase epitaxy GaN using Mg has allowed the realization of blue light emitting diodes.^{3,4} Although much work has been devoted to the study of the properties of Mg impurities in GaN samples, the electronic and optical properties of Mg impurities remain controversial and inconclusive. In this letter, we report the observation of electronic Raman scattering (ERS) in Mg-doped GaN. Our experimental results provide an important information about the electronic structure of Mg impurities in GaN; namely, the energy difference between the ground

and first excited states of Mg impurities in GaN is about one-half of its binding energy.

The Mg-doped wurtzite GaN samples studied in this work were grown by molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) techniques on (0001)-oriented sapphire substrates with about 1- μm -thick AlN buffer layers. The thickness of GaN layers was about 2 μm . The *z* axis of this wurtzite structure GaN is perpendicular to the sapphire substrate plane. The Mg concentrations were $N_{\text{Mg}} \cong 10^{19} \text{ cm}^{-3}$, $5 \times 10^{18} \text{ cm}^{-3}$ for MBE and MOCVD-grown samples, respectively, as determined by secondary ion mass spectroscopy (SIMS) experiments. The free hole concentrations were $3 \times 10^{17} \text{ cm}^{-3}$, $1 \times 10^{17} \text{ cm}^{-3}$ for MBE and MOCVD-grown samples, respectively, which were measured at $T=300 \text{ K}$ and by Hall measurements.

Raman scattering experiments were carried out by using the second harmonic of a mode-locked continuous-wave (cw) yttrium-aluminum-garnet (YAG) laser operating at a repetition rate of about 76 MHz. The laser pulse width was about 80 ps and photon energy was about 2.34 eV. This excitation laser, which had an average laser power of about 200 mW, was focused into the samples with a spot size of about 100 μm . Raman scattering measurements were made in a variety of scattering geometries; however, we shall only present results for $Z(X,X)\bar{Z}$, $Y(X,X)\bar{Y}$ scattering geometries, where $X=(100)$, $Y=(010)$, and $Z=(001)$. Raman scattering signal was detected and analyzed by a standard Raman system equipped with a charge-couple device (CCD) as a multichannel detector.

Figures 1 and 2 show two typical Raman scattering spectra for a MBE-grown, Mg-doped GaN sample and a MOCVD-grown, Mg-doped GaN sample, respectively, taken at $T=25 \text{ K}$ and in $Z(X,X)\bar{Z}$ configuration. These two spectra are very similar and are normalized to their respective $A_1(\text{LO})$ phonon intensities. The structure centered around 757 cm^{-1} comes from scattering of light by the E_g phonon mode of sapphire;^{5,6} the shoulder close to 741 cm^{-1} belongs to the $A_1(\text{LO})$ phonon mode of GaN. In addition to these

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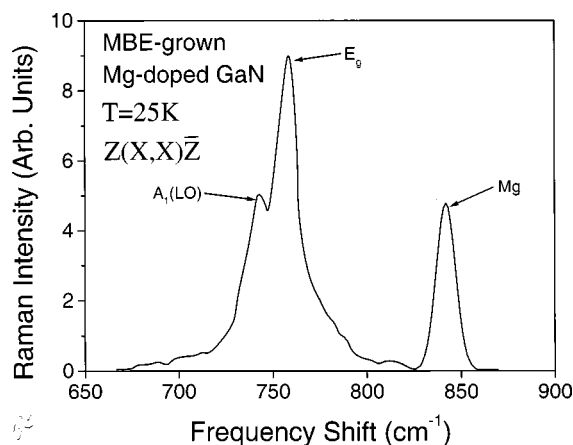


FIG. 1. A Stokes Raman spectrum taken for a MBE-grown, Mg-doped GaN sample. The total Mg concentration is $1 \times 10^{19} \text{ cm}^{-3}$. The structure around 841 cm^{-1} is attributed to the electronic Raman scattering from the neutral Mg acceptors in Mg-doped GaN.

expected phonon modes, there is a well-defined structure showing up at about 841 cm^{-1} ($\cong 105 \text{ meV}$). Because of the following reasons this additional structure was attributed to ERS from neutral Mg impurities in GaN:

- (1) It is well-known that photons can excite holes from ground state to excited states in neutral acceptors in semiconductors—the so-called “electronic Raman scattering.”⁷
- (2) This structure has been observed for both MBE and MOCVD-grown, Mg-doped GaN samples but not for either MBE or MOCVD-grown undoped GaN samples.
- (3) The intensity of the structure has been found to decrease as the lattice temperature increases. This is consistent with our assignment that the structure comes from electronic Raman scattering from neutral Mg impurities and rules out any possible assignments of either overtone or combination modes, whose signal is expected to increase with temperature.
- (4) The observed signal scales quite well with the neutral

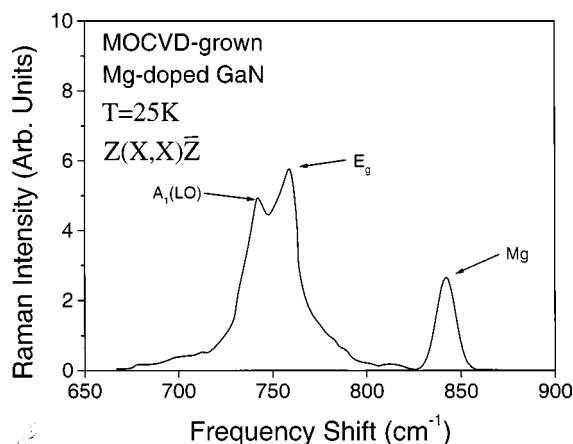


FIG. 2. A Stokes Raman spectrum taken for a MOCVD-grown, Mg-doped GaN sample. The total Mg concentration is $5 \times 10^{18} \text{ cm}^{-3}$. The structure around 841 cm^{-1} is attributed to the electronic Raman scattering from the neutral Mg acceptors in Mg-doped GaN. Figures 1 and 2 are normalized to their respective $A_1(\text{LO})$ phonon mode intensities, so that they are readily compared. The slight decrease in the E_g phonon mode intensity as compared to that in Fig. 1 is due to a slight misorientation in the scattering geometry.

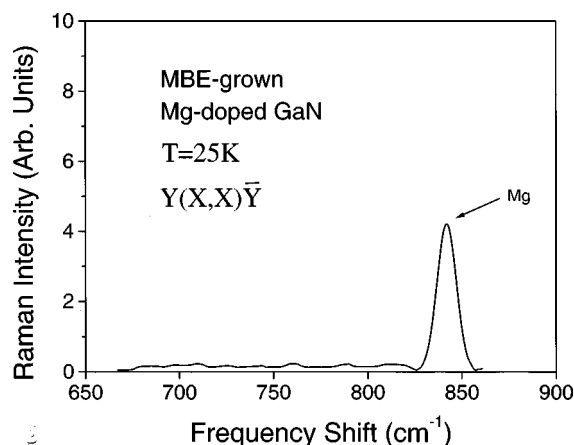


FIG. 3. A Stokes Raman spectrum for the MBE-grown, Mg-doped GaN sample, taken under the same experimental conditions as in Fig. 1 but at scattering configuration $Y(X,X)\bar{Y}$. The structure around 841 cm^{-1} is due to electronic Raman scattering from neutral Mg acceptors.

Mg concentration. As indicated by Figs. 1 and 2, the ratio of total neutral Mg acceptor concentration is about 2 to 1, and the ratio of ERS signal is also about 2 to 1 for MBE and MOCVD-grown samples.

For a shallow acceptor in a simple semiconductor such as Si, in the effective mass approximation, its electronic states are made up of Bloch waves chosen from near the top of the valence band, as a result, ERS signal from the acceptor is expected to show the same polarization symmetry as the main phonon line; in other words, there exists a simple selection rule for ERS signal for a shallow acceptor in a simple semiconductor. In our current situation—Mg impurity in wurtzite GaN, Mg impurity is believed to have relatively large binding energy ($E_{Mg} \approx 200 \text{ meV}$),^{8,9} and therefore it is a relatively deep acceptor; in addition, GaN is a polar, piezoelectric semiconductor with a relatively complicated valence band structure. Therefore, it is rather difficult to deduce a selection rule for ERS signal. Experimentally, what we have found is that ERS signal from neutral Mg impurity is present in all the scattering geometries that we have tested, but with different scattering strengths. For example, Fig. 3 shows a Raman spectrum for the MBE-grown, Mg-doped GaN sample, taken under the same experimental conditions as in Fig. 1 but in $Y(X,X)\bar{Y}$ scattering configuration. No phonon modes associated with either GaN or sapphire are observed in $Y(X,X)\bar{Y}$ configuration in this spectral range, as expected. ERS signal associated with Mg impurities is observed with its intensity comparable to that observed in $Z(X,X)\bar{Z}$ configuration.

We have repeated our Raman measurements with cw lasers having photon energies at 1.92 and 2.42 eV, respectively. The results are very similar to what we have presented using pulsed laser with photon energy at 2.34 eV and repetition rate at 76 MHz. This observation rules out the possibility of the effect of high laser power density used in the presentation.

We note that in addition to the expected Raman signal from GaN, sapphire and ERS, we have also observed two Raman signal very close to 260 and 657 cm^{-1} which has been reported by Harima *et al.*¹⁰ as local modes in Mg-doped

GaN. The intensity of these two modes has been found to be very weak in our experiments—at least one order of magnitude smaller than that of the optical phonon modes in GaN. We believe that the reason why ERS signal from Mg-doped GaN was not observed by previous researchers is most likely due to the quality of Mg-doped GaN samples.

The contribution of ERS signal in semiconductors comes primarily from the transition of hole from the ground ($1s$) to first excited ($2s$) states.⁷ The reported binding energy of Mg impurity in wurtzite GaN ranges from 150 to 255 meV.^{8,9} If we were to use the average value ($\cong 190$ meV) for the binding energy, then our experimental results suggest that the $1s$ – $2s$ transition in the Mg impurity is about one-half of its binding energy.

In conclusion, we have performed electronic Raman scattering experiments on both MBE and MOCVD-grown Mg-doped wurtzite GaN samples. Our experimental results demonstrate that the energy difference between the ground and first excited states of the Mg impurities in wurtzite GaN is about one-half of its binding energy.

This work was supported by the National Science Foundation under Grant No. DMR-9301100.

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