Variation of lattice parameters in GaN with stoichiometry and doping

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Lattice parameters were measured for different GaN samples, undoped as well as doped with Zn or some iron-group metals. Very large variations in values of a and c were obtained, the difference between extreme values being as large as 1%. It appears that nitrogen vacancies V_N cause a decrease in lattice parameters of GaN approximately according to $\Delta a/a \approx \Delta c/c \approx - V_N/N_{GaN}$. An additional increase in lattice parameters at high growth rates is the interpreted as due to self-interstitials in undoped materials. High doping with Zn and some iron-group metals (Fe, Cr, Ni) also causes a large increase of lattice parameters, possibly due to a substantial incorporation of these elements at interstitial sites and at N sites.

I. INTRODUCTION

The lattice parameters of a solid material are experimentally easily accessible quantities. They are also fundamental properties of the material, since a great many physical properties depend parametrically on the lattice constants in a simple way. The defect concentration is perhaps the most important factor in determining the transport properties of a semiconducting material. Therefore, it seems surprising that the relationship between defect concentration (including point defects, such as vacancies or interstitials, complexes involving more than one lattice site, or extended defects such as dislocations) and lattice parameters has only received some scattered attention in literature. At present there seems to be no firm theory to predict the influence of such defects on lattice parameters. Quite contradictory such predictions exist, e.g., on the influence of vacancies on lattice parameters of semiconductors.[1-4] The experimental situation seems to be equally confusing. It is easy to find even a difference in sign of the change in lattice parameters from different experiments performed on different samples due to a nominally similar introduction of defects in the material.[5-7] It seems clear that more work in theory as well as experiment will be necessary to get a reasonable picture of this important area of defect properties.

The lattice parameters for the wurtzite III-V compound GaN have been investigated previously by a large number of authors using material grown by different techniques. A remarkably large scatter in values has been reported, with a values ranging from 3.160 to 3.190 Å and c values ranging from 5.125 to 5.190 Å for nominally undoped material.[8-28] A synopsis of such previous data is given in Table I. This scatter in data is much larger than the accuracy of determination involved in at least a major portion of these investigations.

It is therefore reasonable to assume that the scatter in lattice-parameter data for GaN evident from Table I is mainly due to differences in growth conditions and, consequently, in defect concentration. To verify this assumption, and to get some insight into the mechanisms underlying this surprisingly large scatter, we have undertaken a comparative study of lattice parameters for a large number of GaN samples, undoped as well as doped, and grown under varying conditions.

Growth and relevant properties of the GaN material used in our experimental study, as well as the procedure of measuring lattice parameters of the samples, will be described in Sec. II. Experimental results for lattice parameters of undoped and doped samples are presented in Sec. III. In

TABLE I. Review of lattice-parameter values for GaN at room temperature from different sources in literature.

a (Å)	c (Å)	Ref.
3.189	5.185	8
3.18	5.16	9
3.180 ± 0.004	5.166 ± 0.005	10
···	5.185 ± 0.0006	11
3.186	5.178	12
3.180 ± 0.001	5.178 ± 0.002	13
3.18 ± 0.02	5.19 ± 0.02	14
3.182 ± 0.001	5.176 ± 0.002	15
3.190 ± 0.002	5.190 ± 0.002	16
3.190 ± 0.005	5.17 ± 0.01	17
3.190	5.184	18
3.160 ± 0.008	5.125 ± 0.010	19
3.182	5.173	20
3.180	5.166	21
3.190	5.189	22
3.1683	5.1381	23
3.182 ± 0.003	5.173 ± 0.003	24
3.188	5.190	25
3.17 ± 0.02	5.16 ± 0.021	26
3.182	5.173	27
3.18	5.18	28

Sec. IV the obtained results are discussed in more detail and connected with the defect properties of the GaN material used. A comparison is also made with previous results on variation of lattice parameters with defect concentration for other semiconductors. The most important conclusions from this work are listed in Sec. V.

II. MATERIALS AND EXPERIMENTAL PROCEDURE

The material used for this investigation was grown by vapor-phase epitaxy on (0001) sapphire substrates, as described separately.[29,30] The deposition temperature was kept at 1025–1050 °C, and growth rates (of layer thickness) were varied from very low values up to as much as 10 μm/min. This was achieved by controlling gas flow rates and the position of the substrate in the deposition zone. Dopants were incorporated during growth by vapor transport. Most GaN layers referred to in this paper had a thickness of about 100 μm. This was necessary to ensure good-quality GaN material, since particularly at high growth rates a large defect (dislocation) concentration can occur in the region close to the substrate, sometimes extending as much as about 5 μm away from the substrate (Fig. 1). The preparation of samples for x-ray investigations had to include a polishing step to remove the entire sapphire substrate. In addition, the part of the GaN layer closest to the substrate was removed to leave only GaN samples of proper crystalline perfection for x-ray investigations. These samples were finally ground to powder prior to lattice-parameter measurements.

Crystallographic investigations were performed with a Guinier camera. To get an accurate determination of a and c values for the GaN unit cell, filtered monochromatic Cu $K\alpha_1$ radiation was employed. Further, a KCl reference was mixed with the GaN sample. A very accurate densitometer evaluation technique for determination of line positions on the film (normally used for spectroscopic purposes) was available, which allowed good precision in computer evaluated data for a and c parameters.

III. EXPERIMENTAL RESULTS ON LATTICE PARAMETERS

Results from our measurements from 15 different GaN samples are shown in Table II. Two groups of samples were studied. $U1$–$U5$ are nominally undoped samples, which should be representative for an evaluation of variation of lattice parameters from growth conditions alone. A second group of samples, $D1$–$D7$, are doped with iron-group metals such as Fe, Cr, Ni, and Cu. Such

dopants cause deep levels in the band gap, which are found to affect electrical compensation of GaN.[30] Their possible additional effect on lattice parameters should emerge from the data in Table II. The last group of samples, $D8$–$D10$, are Zn doped, and are included to show the effect of rather high Zn concentrations on GaN
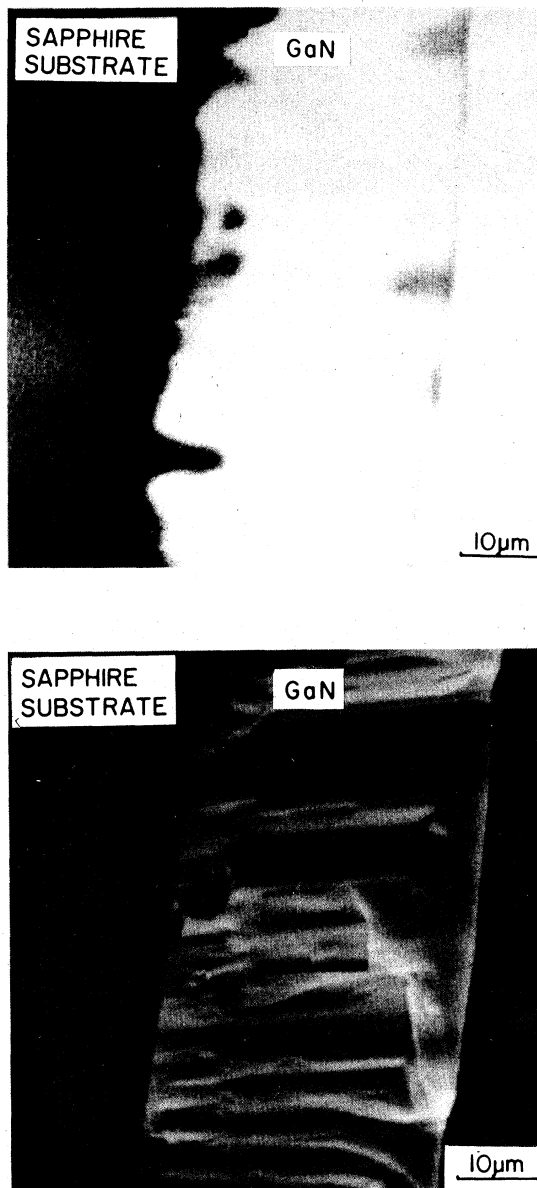

FIG. 1. SEM cathodoluminescence topograph of a cleaved edge of an undoped GaN layer (a), compared to the corresponding SEM surface picture (b). Within a few μm of the substrate, the GaN material has a high defect density, and therefore shows very low luminescence intensity.

lattice parameters.

The data from the group of undoped samples in Table II indicate that variations in growth conditions have a quite remarkable influence on lattice-parameters for GaN. Samples $U1-U3$ represent good quality layers, about 100 μm thick, with carrier concentrations below 10^{19} cm^{-3} (300 K) and mobility about 100 cm^2/V sec (300 K). The total detected impurity concentrations in these layers were found to be less than 50 ppm (if rather large amounts of Al normally incorporated in concentrations 100–1000 ppm are disregarded),[31] from an analysis with secondary-ion mass spectrometry (SIMS). (Some crystals were found to have an impurity content much lower than these stated maximum values.) It is evident from Table II that such samples show no significant scatter in a values. There is, however, some variation in c values for these layers, which indicates a layer sensitivity of c values for crystal-growth parameters. Such behavior has previously been observed for ZnO.[32] Samples $U4$ and $U5$ represent extreme growth conditions. $U4$ was grown very rapidly (growth rate about 10 μm/min, compared to about 1 μm/min for samples $U1-U3$) and was found to have a bad crystalline perfection (polycrystalline, high dislocation density). Sample $U5$, on the other hand, was a layer grown very slowly (at a rate <0.1 μm/min). Such layers have a very good crystalline perfection, as shown by recent channeling studies.[33] Their N-vacancy concentration appears to be very high, however, which makes them degenerate n type if undoped (the N vacancy is a shallow donor in GaN)[11]. It thus appears as a high growth rate induces large values for the lat-

tice parameters, while consequently low growth rates give low values for both a and c. The difference between our extreme values ($U4$ vs $U5$) is about 1%, which is at least an order of magnitude larger than the largest corresponding shifts reported in GaAs.[7]

Our observations on the influence of growth rate on lattice parameters for undoped vapor-phase epitaxy (VPE) grown GaN material are in agreement with the trend that can be observed in the collection of data from previous investigations presented in Table I above. The lowest values for lattice parameters in Table I are for samples grown as powder, where normally very slow growth rates (say <0.1 μm/min) are obtained.

No systematic study of the influence of doping on lattice parameters of GaN was carried out, since inadvertent contaminants are still a problem in the present technique of GaN VPE growth. Since iron-group transition metals were found to have interesting effects on the electronic properties of the material,[30] we have included material doped with iron-group metals in our analysis of lattice parameters. The results are shown by the second group $D1-D7$ in Table II. Samples $D1-D3$, $D6$, and $D7$ in this group are grown with a growth rate about 1 μm/min, i.e., about the same as for $U1-U3$ described above. Comparing these sets of data, it seems evident that these iron-group contaminants cause a lattice dilation in GaN. A SIMS analysis shows that the main contaminants in the crystals $D1-D3$, $D6$, and $D7$ were Fe and Cr, both present in concentrations of 20–100 ppm. Al was present in concentrations 500–1500 ppm, which should have a negligible effect on lattice parameters if

TABLE II. Measured values for lattice parameters a and c at 20 °C for different undoped ($U1-U5$) and doped ($D1-D10$) GaN samples grown by VPE on sapphire. The uncertainties indicated here are the standard deviations obtained in the computer evaluation of data from about ten lines on the film.

Sample	a (Å)	c (Å)	c/a
$U1$	3.1865 ± 0.0002	5.1822 ± 0.0003	1.6263 ± 0.0002
$U2$	3.1866 ± 0.0007	5.1875 ± 0.0012	1.6279 ± 0.0007
$U3$	3.1865 ± 0.0007	5.1869 ± 0.0012	1.6278 ± 0.0008
$U4$	3.1988 ± 0.0004	5.2024 ± 0.0011	1.6264 ± 0.0006
$U5$	3.1683 ± 0.0006	5.1483 ± 0.0021	1.6249 ± 0.0009
$D1$	3.1961 ± 0.0010	5.1939 ± 0.0023	1.6251 ± 0.0013
$D2$	3.1968 ± 0.0002	5.1972 ± 0.0005	1.6258 ± 0.0003
$D3$	3.1931 ± 0.0005	5.1913 ± 0.0018	1.6258 ± 0.0008
$D4$	3.2037 ± 0.0004	5.2106 ± 0.0007	1.6264 ± 0.0004
$D5$	3.1970 ± 0.0007	5.1976 ± 0.0015	1.6258 ± 0.0011
$D6$	3.1958 ± 0.0004	5.1925 ± 0.0010	1.6248 ± 0.0005
$D7$	3.1916 ± 0.0004	5.1913 ± 0.0014	1.6265 ± 0.0006
$D8$	3.1912 ± 0.0001	5.1902 ± 0.0005	1.6264 ± 0.0002
$D9$	3.1924 ± 0.0005	5.1928 ± 0.0011	1.6266 ± 0.0006
$D10$	3.1936 ± 0.0006	5.1965 ± 0.0011	1.6272 ± 0.0007

Al is incorporated on the Ga site. (Note that lattice parameters of GaN and AlN are very similar.[22]) Sample $D4$ has a similar doping, but is grown with a growth rate about 10 μm/min, i.e., similar to $U4$. The extremely high values for a and c observed for $D4$ are therefore due to an excessive growth rate in addition to doping. Sample $D5$ is a crystal grown at normal growth rate (≈ 1 μm/min), but intentionally doped with a high Ni concentration. The data obtained for $D5$ (Table II) show that Ni behaves similarly to Cr and Fe in dilating the GaN lattice.

Zn doping has been employed for the purpose of preparing high-Ohmic GaN for light emitting devices,[34] and is of great interest because of the different electronic levels caused by Zn in GaN, making light emission over the entire visible spectrum possible.[35-37] Sample $D8$ is a Zn-doped layer grown rather slowly ($\approx 0.1 \mu$m/min) with a rather high crystalline perfection. The lattice parameters of $D8$ clearly exceed the corresponding values for undoped material, which means that Zn doping expands the GaN lattice. The same conclusion is drawn from the results of $D9$ and $D10$. These layers were so called in-structures, i.e., a Zn-doped layer was grown on top of a nominally undoped GaN layer, all with a growth rate of about 1 μm/min. The values shown in Table II are obtained as an average over the broadened double lines observed in these cases. Indeed, if Zn doping causes an increase in lattice parameters, a double line would be expected to occur in a composite sample such as $D9$ and $D10$, where undoped material is also admixed. An example of such a double line is shown in Fig. 2. If the two sets of lines are evaluated separately, we obtain, e.g., for sample $D10$ values $a = 3.190$ Å and $a_{Zn} = 3.197$ Å for undoped and Zn-doped material, respectively. The value $a = 3.190$ Å is typical for rather rapidly

FIG. 2. Comparison between the appearance of diffraction lines on the film for two different samples ($D5$ and $D10$). $D5$ is a homogenous layer, while $D10$ is an in-structure with Zn-doped GaN on top of nominally undoped GaN. $D10$ shows a double line interpreted as being due to an increase of lattice parameters in the Zn-doped part of the layer.

grown undoped material (cf. $U1-U3$ above). Incorporation of about 10^{20} cm^{-3} Zn, therefore, seems to cause an increase in lattice parameters of about 0.2%.

The possible variation of lattice parameters within a particular sample can be judged from the linewidths observed on the films. Except for $D9$ and $D10$ discussed above, very narrow lines were observed in all cases (Fig. 2). This means that such variations over the sample were small; the area of the layer used for each sample was also rather small, 5–10 mm^2. The fact that the lattice constants are very well defined within a sample, together with the large variations observed between different samples (which will be shown below to be systematic in defect concentration), is a good argument that the large variations in lattice parameters are indeed created during growth of the material, and not due to strains or dislocations created during the sample preparation after growth (such as the grinding step). Even though the grown in dislocation density well away from the substrate (see above) could still be of the order 10^5 cm^{-2} (Ref. 18), we again think the narrow linewidths give a good argument that possible variations in dislocation density of the layers do not contribute the major effect (of the order 1%) on the variation of lattice parameters shown above.

IV. DISCUSSION

To our knowledge variations of room-temperature lattice parameters of the magnitude of 1% were previously unheard of for semiconductor materials. Usually such variations, as reported for the most common semiconductors such as Ge, Si, and GaAs, are less than 10^{-4} and typically a few ppm.[5,38-42] Similar accurate investigations for the more exotic III-V compounds or II-VI compounds seem to be absent, but there is certainly some scatter in published data also for such materials,[43,44] although not as large as demonstrated here for GaN. Our data clearly demonstrate that accurate evaluation of crystallographic data has to consider the defect properties of the particular sample under study. Sizable variations seem to occur with growth conditions for undoped material, which is therefore interpreted as an influence of native defects such as vacancies. Doping with Zn and iron-group impurity atoms was also found to influence the lattice constants quite drastically for GaN. We will discuss these "intrinsic" and "extrinsic" influences on lattice parameters in somewhat more detail below.

It has previously been established that the conductivity of not intentionally doped GaN prepared in the manner described above is generally not due
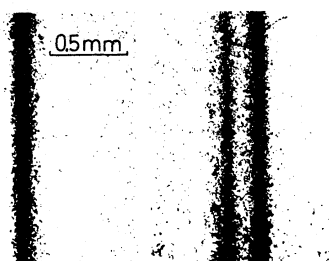
to the incorporated impurities, but rather to the creation of native defects.[11,29] The material has a tendency to become low-restitivity n type, with an electron concentration far above detected levels for impurities.[11] The most obvious candidate for a shallow donor state causing these effects is the nitrogen vacancy V_N. V_N is expected to behave as a donor in GaN, just as V_{Ga} should be an acceptor.[45] (A corresponding situation seems to have been experimentally proved for GaAs, where V_{Ga} is an acceptor and V_{As} a donor.[46]) Furthermore, other intrinsic defects such as antisite defects are calculated to have much higher energies of formation in GaN than the single vacancies, and the latter would therefore be expected to be the important species even after a cooling down to room temperature.[45] Therefore, we have confidence in the assumption that the n-type conductivity of undoped GaN is due to the isolated V_N donors, which seem to have a shallow binding energy of about 30 meV.[29,47]

Independent of the data reported here, we have observed a definite correlation between the growth rate of the epitaxial GaN layers and their electron concentration. Very slowly grown (<0.1 μm/min) layers always come out degenerate n type if undoped, with electron concentration (300 K) of typically $5 \times 10^{19} - 10^{20}$ cm^{-3}. A higher growth rate always reduced the electron concentration n; a rate of about 1 μm/min at 1050 °C was found to reduce n well below 10^{19} cm^{-3} at 300 K for undoped layers. This is consistent with previous data taken over a very limited range of growth rates.[11] (With acceptor doping with, e.g., Zn, high-resistivity material can easily be obtained even for low growth rates.[29,48]) At low growth rate, a high V_N concentration is apparently created in undoped material grown at about 1050 °C. This is not surprising in view of our present knowledge about the thermal instability of GaN. In some previous investigations, thermal instability has been reported for temperatures as low as 800 °C.[49] Our results further indicate that (for growth rates below 1 μm/min) the more rapidly the growth is taking place, the larger is the difference between deposition and dissociation rates, which results in a reduced V_N concentration.

Our data on lattice parameters for undoped GaN reported here establish the relation between growth rates and values of a and c. The above discussion strongly indicates that the physical correlation involved is the one between lattice parameters and V_N concentration. Our interpretation is that a large V_N concentration, say of the order 10^{20} cm^{-3}, corresponding to a very low growth rate (<0.1 μm/min) has the remarkable property of reducing the lattice constant more than 0.5% below the value

typical for layers grown at about 1 μm/min, where V_N is estimated to be less than 5×10^{18} cm^{-3}. From early measurements on nonstoichiometric GaAs a similar variation of lattice parameters on V_{As} concentration was claimed.[7] In their case a relation $\Delta a/a \approx V_{As}/N_{GaAs}$ was found to hold up to $\Delta a/a \sim 10^{-4}$; at higher V_{As} concentration a saturation in $\Delta a/a$ occurred.[7] Note that for GaAs an *increase* $\Delta a/a$ with V_{As} concentration was claimed.[7] In our case with GaN we find a *decrease* in a and c with V_N concentration, approximately $\Delta a/a$ ($=\Delta c/c$) $= -V_N/N_{GaN}$. This is the result obtained from the empirical Vegard's law arguments,[50] generally used in the discussion of the influence of point defects on lattice parameters. If we put

$$\Delta a/a = (4/\sqrt{3})(\Delta r/a) V_N/N_{GaN} ,$$

where Δr is taken as an appropriate N radius in GaN (estimated as an average of covalent and ionic contributions[51]), we obtain $\Delta a/a \approx -V_N/N_{GaN}$.

Unfortunately, the crude estimates from Vegard's law seem to be of little value when it comes down to the detailed physical mechanisms involved. The major problem is that there are good theoretical arguments for a rearrangement of bonds at a vacancy so as to produce an outward relaxation of the lattice at a vacancy.[45,52] At first sight this would imply that all vacancies expand the lattice, which would fit some experimental data on V_{As} in GaAs,[7] but is in contradiction to our data on V_N in GaN. Our results would indicate that either there is an inward relaxation around V_N in GaN or there are long-range strain fields around such a vacancy, causing a substantial net contraction of the lattice. Further theoretical work is needed to resolve which of these possibilities is correct.

The upward deviations from the "normal" values for the GaN lattice parameters (as represented by, e.g., $U1-U3$ in Table II) are also very large. Such deviations occur for undoped samples grown at a very high growth rate, but also for samples doped with some iron-group metals, Zn, and Mg.[18] For the undoped samples it is reasonable to assume that a large concentration of self-interstitials could be created. Independent experimental support for such an argument is given by recent channeling experiments on VPE GaN.[33] It was found that for crystals grown at a very low growth rate, a high crystalline perfection is obtained. This means that the concentration of interstitials is low (the channeling method does not detect vacancies). For crystals grown at a higher growth rate, a higher concentration of atoms at interstitial sites was always detected.[33] The notion that interstitials would have a tendency to increase the lattice parameters seems to be generally accept-

ed, and appears to be a very reasonable assumption. No quantitative estimates of concentrations of interstitials in the sample $U5$ (and $D5$) relevant for this discussion can be made at present.

The problem of predicting the influence of doping with foreign atoms on lattice parameters seems to be a controversial one, and quite contradictory suggestions appear in literature. The most general idea is the one of atomic size, based on Vegard's law, predicting lattice dilation if the (covalent) radius of the impurity atom is larger than the one it replaces.[50] In partly ionic materials, such as III-V compounds, additional factors have been proposed to influence lattice parameters, such as effective charge-compensation ratio.[53] In the latter case, however, there seems to be a controversy of sign for this contribution in GaAs.[53] In our case of iron-group metals as well as group-IIB metals, an introduction of these on Ga sites would cause a reduction of the lattice parameters according to Vegard's law, since their atomic radius (covalent as well as ionic radius) is smaller than for Ga. This is contrary to the observations reported here. Ionic charge effects could well be important in the case of GaN, but as noted above no firm predic-

tions seem possible in this case.[53] For group IIB metals previous independent data on electrical properties of Zn-doped GaN have led to the suggestion that Zn predominantly occupies vacant N sites when introduced in large concentrations.[54] This would be consistent with the above data on lattice parameters, since the simple size arguments predict a lattice dilation when Zn enters N sites. A similar explanation of our data for the iron-group metals (Fe, Cr, Ni) studied here can be offered if they preferentially occupy nitrogen sites (i.e., they fill out N vacancies). This would also explain the ability of these metal impurities to effectively compensate the V_N donors in GaN to make the material highly resistive.[30]

In spite of the large variations of a and c between different samples grown under different conditions, the c/a ratio was found to vary much less, within the limits 1.6264 ± 0.0015, as evidenced from Table II and Fig. 3. This can be interpreted as a strong stability of the GaN wurtzite structure against variations in defect concentrations and variations in growth conditions. The stability of the wurtzite structure of GaN can be related to the deviation of c/a from the ideal value 1.633.[55] We have never observed cubic GaN in our growth of several hundred GaN epitaxial layers; the same conclusion comes from a parallel investigation of freely nucleated GaN single crystals.[15] Cubic GaN has been reported in literature,[56] but this observation has apparently not been reconfirmed.
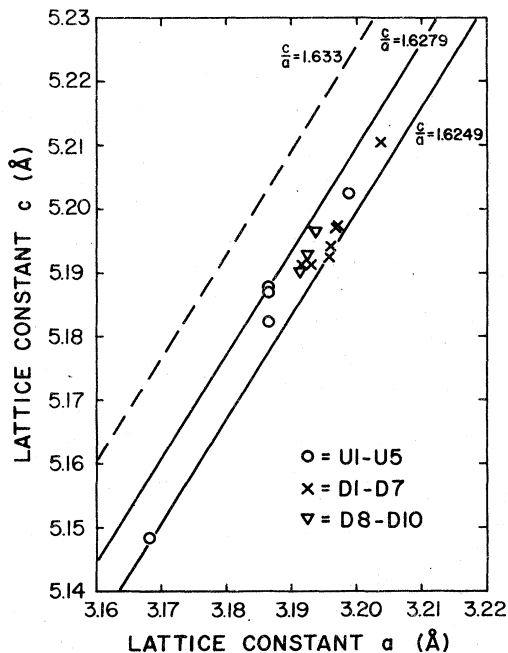

FIG. 3. Synopsis of lattice parameters c and a for all investigated samples of GaN. Undoped samples are denoted (O), Zn-doped samples ($\triangledown$), and iron-group metal doped samples ($\times$). The two full lines (——) correspond to the extremal c/a values observed. The ideal c/a value 1.633 is also shown by the upper line (- - -), showing that all the observed c/a values for GaN fall well below this value.

V. CONCLUSIONS

Accurate measurements of lattice parameters a and c for wurtzite GaN epitaxial layers reveal surprisingly large variations with stoichiometry, as well as with doping with group IIB and iron-group metals. Undoped layers grown slowly (<0.1 μm/min) at 1050 °C are degenerate n type due to a large concentration V_N of N vacancies. This leads to a drastic reduction in lattice parameters, approximately according to $\Delta a/a \approx \Delta c/c \approx - V_N/N_{GaN}$. Very high growth rates at 1050 °C lead to increased values for a and c, partly due to a reduction in V_N, but at high growth rates also due to an increased concentration of self-interstitials. Variations in a and c obtained with undoped layers are therefore found to be in excess of 1% at varying growth conditions.

Doping with Zn leads to an increase of a and c, such that 10^{20} cm^{-3} Zn atoms cause a lattice dilation of about 0.2%. This dilational effect is not entirely due to an incorporation into interstitial sites, but also to a large extent at N sites. Doping with Fe, Cr, or Ni in concentrations 2×10^{18}–10^{19} cm^{-3}

causes lattice dilation of the order 0.1%. The simple Vegard's law arguments imply that the major part of these elements cannot be incorporated on Ga sites.

The collection of data obtained here exhibit a moderate variation of the c/a ratio within the limits 1.6264 ± 0.0015. This is well below the ideal c/a ratio 1.633, indicating a strong stability of the GaN wurtzite structure, even with drastic variations in defect properties. Cubic GaN would therefore not be expected to form under these growth conditions (1025–1050 °C, normal pressure, i.e., far below equilibrium pressure).

ACKNOWLEDGMENTS

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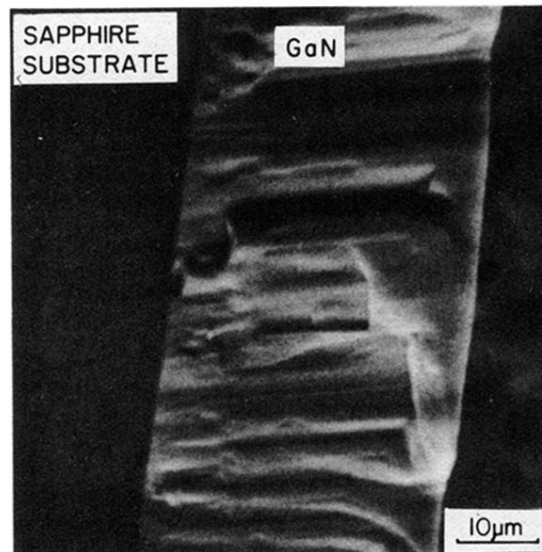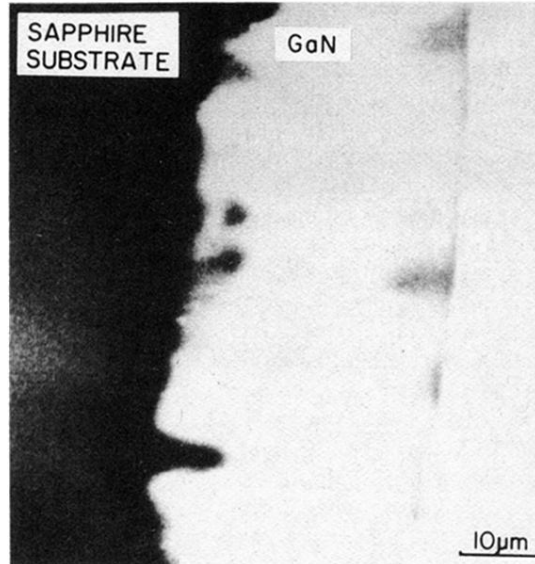[56] W. Seifert and A. Tempel, Kristall. Tech. 9, 1213 (1974).

FIG. 1. SEM cathodoluminescence topograph of a cleaved edge of an undoped GaN layer (a), compared to the corresponding SEM surface picture (b). Within a few μm of the substrate, the GaN material has a high defect density, and therefore shows very low luminescence intensity.