Local electronic structure of Cu-doped GaN investigated by XANES and XLD

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Abstract

X-ray Absorption Near Edge Structure (XANES) and X-ray Linear Dichroism (XLD) measurements of a series of Cu-doped GaN samples with different doping concentrations have been investigated at the Ga and Cu K-edge to get insight into the preferred occupation site of Cu in the GaN matrix. No influence of the Cu concentration in the XANES spectra at the Cu or Ga K-edge could be observed within the resolution of the experiment. γ-Cu_9Ga_4 compounds that formed on the samples during the GaN growth process could be partially removed by etching with HNO_3 but remained to dominate the XANES spectra at the Cu K-edge. For the XLD signals at both absorption edges a clear signal intensity increase after etching could be observed as a consequence of the removal of the Cu_9Ga_4 compounds. The XLD data of the Cu-edge clearly demonstrates that Cu is incorporated in the GaN film. By performing simulations which are compared to the experimental data it was possible to show that most Cu in the GaN film is incorporated on Ga or

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Preprint submitted to Phys. Rev. B *April 8, 2011*

interstitial sites and only a minor fraction on N sites.

Key words: XANES, XLD, GaN, Cu doped nitrides, dichroism

1. Introduction

Cu-doped group III nitrides have recently earned great interest due to the experimental evidence of ferromagnetism observed in GaN [1] and AlN [2] at room temperature. The usage of Cu as a dopant, which is a non-magnetic element, excludes the possibility of magnetic clusters built by the dopant. Therefore the occurrence of ferromagnetism in GaN:Cu does not origin from either Cu or GaN, but is a result of the interaction between the host material and the dopant.

In literature theorists concerned with the study of ferromagnetic Cu-doped GaN have foremost assumed Cu atoms on substitutional Ga sites, e.g. [3–6]. For instance, Wu et al.[3] explain that incorporation scenarios other than Cu substituting Ga sites are not taken into account because they are energetically unfavored. Seong et al.[7] stating ferromagnetism in Cu-doped GaN nanowires show by Anomalous X-ray Scattering that Cu atoms substitute on Ga sites. However, it is still unclear to whan extent Ga sites are occupied and whether N or interstitial sites also play a role in Cu incorporation. Further, since most growth processes of doped GaN do not take place in an equilibrium environment, the occupation of unfavorable energetic states may not be excluded. Because the microscopic mechanism of this system's ferromagnetism is still not fully understood it is of particluar interest to clarify the basic question of the positioning of Cu in the GaN matrix.

The aim of the present work is to understand how Cu is incorporated in

GaN. XLD provides a convenient opportunity to probe the local structural and electronic properties of the Cu atoms in the nitride host, since it is proportional to the anisotropic unoccupied density of charge. The XLD spectrum is therefore highly sensitive to the local symmetry and gives a unique signature in the case of wurtzite structure. Furthermore, to elucidate how Cu atoms are incorporated in the nitride host, i.e. if Cu atoms are substitutional, interstitial or both to the host material, the measured data is compared to simulations.

2. Experimental procedure

The investigated samples were grown at the Karlsruhe Institute of Technology (KIT) by plasma-assisted molecular beam epitaxy (PAMBE). A series of six GaN:Cu samples with varying nominal Cu concentration from 0% to 2.69%, in the following labelled A(0%), B(0.50%), C(1.35%), D(1.77%), E(2.22%) and F(2.69%), was produced. The term "nominal concentration" used here refers to the flux ratio of Cu atoms to the total metal atom flux of Cu and Ga. Assuming sticking- and incorporation coefficients to be the same for Cu and Ga and equal to unity, these numbers would represent an estimate of the actual doping concentration of Cu. However, these assumptions are not justified and hence, the nominal concentration can only be seen as a measure of the relative flux provided during growth. As will be described later, a significant part of the provided Cu atoms form metal compounds in the samples, i.e. not all the provided Cu is available as doping material in the GaN film. In this series of samples, sample C with 1.35% nominal Cu doping takes in a special position due to the measured ferromagnetism. The

data is not shown here, but its magnetic behaviour as well as the growth procedure applied is very similar to the case reported earlier [8].

To obtain better thermal coupling during growth, C-plane oriented sapphire substrates were mounted onto silicon using indium as an adhesive. Each substrate was first outgased in a baking chamber at 130°C for 60 min before introducing it into the growth chamber. It was then heated to 890°C for 30 min for a final outgasing step before nitridation commenced for 180 min at 200°C. A thin AlN buffer layer (thickness $\approx 22 \pm 4$ nm as measured by Scanning Electron Microscopy (SEM)) was introduced prior to the growth of the epitaxial Cu-doped GaN layer. A growth rate of roughly 70 nm/h was used, resulting in GaN film thicknesses in the range of 130-150 nm. After unloading the sample from the MBE system, it was cut into parts, one of which was etched and one left unetched. The etching of the samples was performed to remove metal compounds from the samples and included 65% HNO_3 treatment for 5 min and rinsing with deionised water. To obtain an understanding of the effect of etching on the samples their surfaces were investigated by SEM.

For all samples the XANES and the XLD spectra were measured at the K-edges of Ga and Cu. These measurements were performed with hard x-rays from the ID12 beamline at the European Synchrotron Radiation Facility (ESRF) detecting the total fluorescence yield. The experimental chamber contains eight silicon photodiodes arranged in a semi sphere around the sample that are equipped with 10 μm thick Ni filters. A quarter wave plate was used to flip the linear polarization of the synchrotron light from vertical to horizontal when performing the XLD measurements, also described in detail

in [9]. The angle of incidence was between 14° and 17° with respect to the sample surface. The spectra were simulated using the FDMNES code [10] applying the multiple scattering formalism within the muffin-tin approximation. A supercell of $4 \times 4 \times 4$, i.e. a total of 256 atoms, with a calculation radius of 10 Å was used. For the x-ray absorption spectra eight different doping concentrations were calculated, the lowest possible ranging from 0.78% (with 1 Cu atom in the supercell) up to 6.25%.

3. Results and Conclusion

During growth of the Cu-doped GaN samples Cu is not only incorporated in the film but also forms cubic, non-magnetic γ-Cu_9Ga_4 structures according to X-Ray Diffraction (XRD) [1] and Transmission Electron Microscopy (TEM) analysis [11]. Because of the different placement possibilities of the Cu atoms in the sample (in the GaN film or in the γ-Cu_9Ga_4 structures) a clear distinction of the origin of the Cu signal present in the XANES and XLD spectra must be clarified. For this purpose measurements on as grown samples as well as on samples where the surface compounds had been removed by wet chemical etching were compared.

In a first step, an estimate of the Cu incorporation in the GaN film and the γ-Cu_9Ga_4 compounds is made by means of SEM surface analysis. This gives a better understanding for the following analysis because the intensity of the absorption signal is proportional to the amount of atoms present in a specific configuration. While Cu atoms in GaN, if e.g. substituting Ga sites, give a wurtzite type signature, they should give no signal contribution when bound in γ-Cu_9Ga_4 compounds, as a result of the compounds' cubic

symmetry. In a second step the x-ray absorption spectra are examined, first the XANES spectra of the Ga and Cu K-edge are analyzed. Thereby, XANES simulations of Cu-doped GaN, performed for Cu placement on Ga, N and interstitial sites, and of γ-Cu_9Ga_4 compounds are compared to the experimental data. Next, the XLD data is analyzed and again compared to corresponing simulations.

3.1. γ-Cu_9Ga_4 compound coverage

A crude estimate for the amount of Cu present in the surface compounds (Cu_9Ga_4) with respect to the film can be deduced estimating the Cu_9Ga_4 island coverage using SEM images (as seen in Fig. 1) and an averaged height estimate from TEM pictures of the samples [11]. An important assumption included in the following evaluation, namely that all the precipitates visible on the sample surfaces are only composed of γ-Cu_9Ga_4, is justified by the fact that they are all formed during growth, i.e. at a temperature of 790°C. This can be assumed because some of the compounds have been overgrown by a thin GaN film and is supported by TEM data [11]. Further, a mean Cu to Ga ratio with 32.78% Ga in these compounds is assumed in accordance with the phase diagram given in [12].

Fig. 1 (a) shows an SEM image of the unetched sample F where the surface compounds are well visible. The left part of the picture, where black circles surround the structures, is an example of how the estimated surface coverage of Cu_9Ga_4 was taken into account in the calculations. The same sample after etching is seen in Fig. 1 (b) where about 88% of the compounds have disappeared. Table 1 gives an overview of all the Cu-doped samples with their nominal Cu concentration and in each case the values of the volume

percentage of Cu_9Ga_4 in the sample before and after etching along with the relative and absolute decrease of the amount of compounds. The last two columns give the calculated ratio of Cu atoms bound in the compounds with respect to the total metal atom content of the sample (excluding the amount of Cu in the film, as it is known only for sample C). The fact that the amount and size of the Cu_9Ga_4 compounds on the sample surface increases with increasing nominal Cu concentration is clearly reflected in the numbers of Table 1.

Note that the calculated ratio of Cu, forming compounds, to the total metal content is already higher than the provided Cu to metal flux ratio during growth. This is a plausible outcome because the provided flux ratio of Cu and Ga is not the same ratio as is built into the sample. It is a clear indication that the sticking- and incorporation coefficients of Cu and Ga on GaN are different. While the sticking coefficient for Cu can be assumed to be near unity at the growth temperature used in this study, it is well known to be less for Ga. It is therefore impossible to deduce a reliable number for the Cu concentration in the GaN film by this kind of analysis. However, using results obtained by Wavelegth Dispersive X-ray Spectroscopy (WDXS) on a 1.38% nominally Cu doped sample, where 0.26% of the metal atoms in the GaN film were Cu atoms [11], we can deduce a 'real' doping of 0.24% Cu for sample C assuming the same Cu incorporation rate for both these samples. This means, considering the presence of Cu_9Ga_4 compounds, that approximately 3.1% of the Cu atoms in the sample are incorporated into the GaN film, whereas the remaining roughly 96.9% are found in the compounds. The situation appears reversed when calculating the percentage of Ga in the

film and in the compounds, where we estimate numbers of 96.5% and 3.5%, respectively.

As a first outcome of these estimates, although they may be very rough, we can hold that almost all the Cu that is present in the samples is incorporated in the compound of γ-Cu_9Ga_4. In the next step this will be examined more closely by the much refined technique of XANES and XLD.

For the analysis of the XANES and XLD spectra keep in mind that the illuminated sample area is much larger than the size of a surface compound and also much larger than the mean distance between the compounds. The x-ray signals collected are therefore an average of the sample and do not probe parts of the sample locally. In addition, the hard x-rays of the synchrotron are assumed to penetrate the samples completely, leading to a probing of the whole volume of the samples instead of only the surface layers.

3.2. XANES of the Ga K-edge

Fig. 2 shows XANES spectra of the samples at the Ga and Cu K-edge. Fig. 2 (a) depicts the Ga K-edge XANES spectra of all six samples with different Cu concentrations. The experimental data shows hardly any variation for the different doping concentrations. This is expected, because the amount of Cu incorporated in the lattice is small leading to even smaller differences in the incorporation amount from one sample to another which should not affect the Ga signal of the film a great deal. The large deviations in the higher energy region of samples A(0.00%), B(0.50%) and D(1.77%), marked by "$\times$" in the graph, occur because some crystal lattice planes in the samples satisfied the Bragg condition with respect to the position of some of the detectors. These Bragg peaks are only avoidable when tilting the sample.

Here however, the peaks are well away from the more interesting region of the spectrum, thereby not causing any confusion identifying the real XANES signal.

In Fig. 2 (b) we compare one of the experimental curves (in this case sample C) to the simulated data. Here, simulation results are shown for pure wurtzite GaN (0% Cu) as well as for GaN with 2 Cu atoms in a $4\times4\times4$ super cell (1.56% Cu) replacing Ga atoms, N atoms and situated as interstitials in the largest void of the GaN matrix. The two Cu atoms are separated by the largest possible distance, thereby avoiding possible clustering effects. The variation of doping concentration in the super cell has almost no influence on the calculated spectra (not shown here). Due to this fact, for reasons of clarity, only the 1.56% doped spectra are plotted here. It is worth mentioning that for related future work calculation time may be shortened by considering smaller super cells.

The comparison of the calculated data to the experimental one in Fig. 2 (b) displays general agreement between the two in a number of points. The main peak around 10383 eV is very well described by all simulated curves apart from the curve for Cu on N sites, which is shifted to higher energies by 2 eV. One might be tempted to explain the high energy shoulder of the main peak by a possible admixture of Cu occupation of N sites in GaN. This case is repeated for the next peak at around 10395 eV, where again the high energy shoulder in the experimental data can be accounted for by the graph with Cu on N sites. However, as these shoulder-peaks in the experimental spectrum are also present in the undoped GaN spectrum, we no further need to analyse the origin of these features in dependence of Cu doping. We assume the lack

of precise matching comes about because of the inaccuracy of the theory and claim that the low percentage of Cu in the GaN film does not noticeable affect the spectrum. Further, the simulations fail to describe more details of the measurement, most noticably the low energy rising edge of the spectrum where a distinct peak in the experimental data is seen. This peak also appears in the calculations but is rather a shoulder. It is most pronounced when Cu occupies interstitial sites in the GaN lattice; its exact origin, however, can not be concluded to be due to Cu, for the same argument as above holds. Ga bound in γ-Cu_9Ga_4 compounds can not be seen to influence the spectrum as the double peak feature in the calculated Cu_9Ga_4 spectrum is completely absent in the experimental data. The calculation of Cu_9Ga_4 was performed for one unit cell (52 atoms) and a cluster calculation radius of 10 Å.

3.3. XANES of the Cu K-edge

The right part of Fig. 2, i.e. the spectra (c) and (d), gives details on the Cu K-edge XANES. The graph in Fig. 2 (c) shows experimental results of the doped GaN samples. Again, as with the case for the Ga K-edge, there is no significant difference visible between the samples with different Cu concentrations. This outcome is not surprising remembering the considerations above involving the SEM images, where we stated that other than for the Ga signal, the Cu signal mainly has its origin from the Cu incorporated in the Cu_9Ga_4 compounds and not from the Cu in the GaN film. The spectrum of sample B may seem to differ from the rest, but with regard to the lower statistics in the experimental data for this sample compared to the others, also apparent in the lower signal to noise ratio, the small deviation to the rest of the samples can be considered insignificant.

Fig. 2 (d) depicts the experimental data as well as the simulated data for 1.56% Cu doped GaN where Cu sits on Ga or N substitutional sites, as interstitials or is bound in Cu_9Ga_4. It can clearly be seen that the shape of the experimental data most decently fits the calculated Cu_9Ga_4 graph. However, the shoulder in the rising edge of the measured data is not accounted for in the Cu_9Ga_4 curve. This aspect could be explained by a slight portion of N sites being occupied by Cu atoms. Unfortunately as can be seen by the strongly Cu_9Ga_4 dominated shape of the experimental data, signals of an admixture of the Cu component coming from the Cu atoms incorporated in the GaN film are highly suppressed, i.e. an experimental curve fit with a contribution of one or more of the GaN:Cu curves can be established but is suject to a large error.

Fig. 3 (a) shows the deconvolution of the experimental data by considering the four possible signal origins. Although an accurate fit is not possible for the entire spectrum, a tendency of Cu site occupation can be extracted from the fit by a principle of exclusion. A good overall fit of the experimental data was achieved for a placement of Cu atoms at 4.0% Ga , 0.6% N and 1.1% interstitial sites; the remaining 94.3% of the signal is attributed to Cu_9Ga_4. This means that for Cu in the film 70% is on Ga, 20% on interstitial and 10% on N sites. Although these numbers are values for the best fit when deconvoluting the experimetal spectrum the error bars are rather large, i.e. similar fits can be obtained with a different occupation of Cu in GaN. To find a range where this is possible, the data was fit with the maximum tolerable Cu fraction in each position of Cu on Ga, N and iterstitial sites. The result is that Cu can occupy between 0 - 6.2% Ga, 0 - 0.8% N and 0 - 6.8%

interstitial sites in GaN within the sensitivity of our measurement and is to 93.2 - 100% present in Cu_9Ga_4 compounds. As can be seen by these numbers the experimental data can also be described when assuming the signal origin to be only from Cu_9Ga_4. This kind of fit is best, when assuming additional strain to the compound and can be seen in the inset of Fig. 3 (b).

Since TEM results have indicated epitaxial growth of Cu_9Ga_4 compounds on GaN, we have also investigated XANES signals of strained Cu_9Ga_4. Different magnitudes of strain have been considered ranging from 0.5% to 20%. The shape of the graph and the main peak position changes with varying strain. Best agreement to the measured data is given in the range of 13 - 15% strain, which is a significant amount of strain. Fig.3 (b) shows a fit of the experimental data considering 14% strained Cu_9Ga_4. The change in Cu occupation distribution, with the best fit value given in brackets, is as follows: 0 - 10.6% (3.3%)for Cu on Ga, 0 - 0.5% (0.5%) for Cu on N, 0 - 7.7% (2.2%) for Cu on interstitial sites and 89.4 - 100% (93.9%) for Cu in metal compounds. Again, regarding Cu in the film only, this means that 54.5% is on Ga, 36.4% on interstitial and 9.1% on N sites. Introducing strain to the compound, the difference of Ga or interstitial site occupation plays a less important role for the shape of the graph. Also, this consideration introduces a better feeling for errors and difficulties connected with the analysis of the data. Worth mentioning is however that in XRD as well as in TEM measurements no indication of strain in the compounds could be found within the measurement sensitivity. As a first conclusion we therefore carefully state that most of the Cu in GaN can be found on Ga sites; a placement of Cu on N sides is not preferred and a large fraction of Cu atoms is built into GaN on interstitial

sites.

The results from this analysis roughly correspond to the results from the SEM considerations above, i.e. from XANES we conclude that 5.7% of the Cu in the sample is in the film whereas from SEM and WDXS analysis it was an estimated fraction of 3.1%. Due to the numerous assumptions leading to these numbers the discrepancy is not surprising. Nevertheless, important information can be gained: Cu is incorporated in the film; Cu is not only incorporated on Ga sites; Cu occupies N sites to a measurable extent. This is a finding that has not been previously reported and may lead to new theoretical considerations of different defects, other than only Cu substitutions on Ga sites.

3.4. XLD of the Ga K-edge

XLD spectra were recorded for the etched and unetched samples at the Ga and Cu K-edge. Fig. 4 depicts the results of these measurements where all the spectra were normalized to the background at the lowest and the highest energies of the spectrum. The sharp peaks in the graphs marked by "$\times$", occurring frequently for the undoped GaN sample in diagrams (a) and (b) and for all the samples in diagrams (c) and (d) just above 9000 eV and around 9035 eV, are Bragg peaks as also mentioned above and deserve no further attention. In part (a) and (b) of Fig. 4 the XLD spectra of the unetched and the etched Ga K-edge are visible, respectively. We can clearly see an increase of the XLD signal for the etched samples compared to the unetched ones. Depending on the sample, the increase of signal amounts to an average of about 7% to 33%. The behavior of the XLD signals' intensity for the different samples and peaks can be seen in Fig. 5. The intensity

variation between etched and unetched samples can be explained by the fact that after etching cubic surface compounds (Cu_9Ga_4) have been removed and a higher percentage of the signal collected origins from the wurtzite film, hence giving more intense peaks in the XLD spectrum. The non-uniformity in the increase of the intensity can be ascribed to the different amount of compounds removed from the different samples, as was also seen in the SEM analysis above (see the absolute $V_{Cu_9Ga_4}$ decrease column in Table 1). The tendency of higher nominally doped samples giving less increase of the XLD signal is presumably due to the short etching time applied. This means that because more Cu supply during growth leads to more compounds, a longer etching time is needed to completely remove the compounds. However, for all samples the etching time was constant leading only to a partial removal of the compounds and in conclusion to a higher percentage of remaining Cu_9Ga_4 on the samples having been exposed to higher Cu fluxes.

Apart from the slight variation in intensity, an examination of the difference in the Ga K-edge XLD signal in dependence of the Cu doping amount allows no further statement. However, comparing the experimental XLD data of the Ga edge to simulations, as is done in Fig. 6 (b), we can state that only a very small percentage of Cu atoms is located on N substitutional sites. This conclusion is drawn from the qualitatively greatly differing curve progression of the simulated data for 2 N atoms having been replaced by 2 Cu atoms in a $4 \times 4 \times 4$ super cell calculation. A clear analysis of a quantitative measure of Cu atoms occupying Ga, N or interstitial sites is not possible at this stage, due to the inaccuracy in modelling these spectra. This inaccuracy can be shown in Fig. 6 (a) where the experimental and simulated data

of pure GaN are depicted. Although a fairly good qualitative agreement is apparent, it shows that the fit is not good enough to discriminate between Cu on Ga or interstitial sites in Fig. 6 (b).

3.5. XLD of the Cu K-edge

The XLD signals of the samples recorded at the Cu K-edge are shown in Fig. 4 (c) and (d). The much lower signal to noise ratio compared to the Ga edge data is clearly visible. Nevertheless, the increase of the signal from the unetched to the etched samples is apparent, again resulting from a lower fraction of compounds present in the samples, thereby being responsible for less absorption of x-rays in the cubic structure (not contributing to the XLD signal). In graph (c) of Figure 4, sample B seems to divert significantly from the rest of the samples. This is however not considered to be of physical origin; rather the behavior is traced back to difficulties in reliably normalizing the data acquired for this sample due to the presence of two intense Bragg peaks and the low statistics compared to the data of the other samples, therefore being responsible for impracticable intensity comparisons. Due to the generally low statistics of the data for all samples, resulting from limited beam time and a low incorporation amount of Cu in the GaN film, a comparison of the signals' intensities with respect to the different doping concentration is unfeasible. However, a clear statement of the presence of an XLD signal is possible, leading to the conclusion that Cu is really incorporated in the GaN film and is not merely present in the from of Cu_9Ga_4 compounds.

Again, the possibility of Cu_9Ga_4 being strained and thereby deviating from its cubic structure, being responsible for the XLD signal has also been considered. The results of simulations performed for up to 20% strained

Cu_9Ga_4 is shown in Fig. 7 (a) and (c) together with the experimental data of sample C (b) for comparison. We consider none of the calculated spectra as in good agreement with the experimental curve and hence consider the possibility of strained Cu_9Ga_4 to be small.

Although the statistics of the experimental data makes a quantitative analysis impossible, an idea of where most of the Cu atoms are placed in the GaN host lattice can be extracted when comparing the experiment to the simulations. Fig. 8 (a) to (c) depicts the Cu K-edge XLD simulation results for 1.56% Cu-doped GaN on Ga, N and interstitial sites; (d) shows the XLD graph for strained Cu_9Ga_4; the mixture of all the components (Ga, N, interstitial sites) according to the same fractions of contributions as described above for the XANES spectra and the experimental data of sample C are shown in Fig. 8 (e) and (f), respectively. The experimental data shows a non-zero XLD signal. As a guide to the eye the two main peaks present in Fig. 8 (f) are marked by dotted lines throughout the other graphs. We observe that the intense first negative peak in the Cu on N sites graph is missing in the experimental data. Hence a large percentage of Cu on N sites can safely be assumed to be limited to a very small amount. Similarly, the Cu on Ga and interstitial sites make a contribution to this first negative peak, but with much lower intensity, therefore not giving up the possibility of a significant percentage of these configurations being present but unresolved in the experimental data. Interestingly, the best matching spectra to the experimental curve is the XLD signature of Cu on interstitial sites where the shape of the maxima correspond well with the two peaks in Fig. 8 (f). The fit to the experimental data, where the composition of the

signal is the same as the one determined by the XANES data (shown in Fig. 3 (a)), also describes the measured XLD data well within the sensitivity of the measurement. Further, the order of magnitude of the signal's intensity is well described in this case where the majority of the signal is assumed to be absorbed by the Cu_9Ga_4 compounds. The fact that the fit results of the XANES spectra correspond well to the XLD spectra is an important check for consistancy and makes the data, in spite of the low signal to noise ratio, reliable.

4. Summary

A series of etched and unetched Cu-doped GaN samples with different doping concentrations have been investigated by XANES and XLD measurements. The experimental data shows no apparent dependence on the Cu concentration in the samples. The XANES spectra at the Cu K-edge are dominated by the signal coming from Cu_9Ga_4 compounds. The XLD data show an increase of signal intensity after etching, due to partial removal of the Cu_9Ga_4 compounds. The observed Cu K-edge XLD signal proves the incorporation of Cu in the GaN matrix. Simulations of GaN with different Cu site occupation possibilities compared to the experimental data show that most Cu in the GaN film occupies Ga or interstitial sites and only little Cu is incorporated on N sites.

5. Acknowledgements

The authors from Karlsruhe acknowledge support from the DFG-Center for Functional Nanostructures, in which part of this work was performed.

One of the autors (RS) would like to acknowledge M. Bürkle for the fruitful discussions on the simulation results.

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Table 1: Listing of the Cu-doped GaN samples with the estimates Cu_9Ga_4 coverage by SEM measurements.

sample	**nom. conc. [%]**	$\mathbf{V}_{Cu_9Ga_4}/\mathbf{V}_{sample}$ [%]		$\mathbf{V}_{Cu_9Ga_4}$ **decrease [%]**	$\mathbf{V}_{Cu_9Ga_4}$ **decrease [mm^3]**	**# Cu at. in Cu_9Ga_4/# metal at. [%]**	
		unetched	etched			unetched	etched
B	0.50	1.46	n.a.			3.47	
C	1.35	3.19	0.81	79.74	3.47×10^{-4}	7.26	1.95
D	1.77	5.72	3.02	65.43	4.13×10^{-4}	12.27	6.89
E	2.22	6.39	2.15	74.84	6.48×10^{-4}	13.51	5.01
F	2.69	11.44	1.56	88.03	15.88×10^{-4}	21.78	3.68

Figure captions:

Figure 1: SEM image of sample F(2.69%) before etching (a) and after etching (b). On the left sides of the pictures the surface coverage of the precipitates is estimated by approximating the structures' area with the area of multiple small circles. For this sample, a 88% decrease in the surface coverage of the surface structures is calculated from the pre-etched to the post-etched condition of the sample.

Figure 2: Experimental XANES spectra of the Ga (a) and Cu (c) K-edge for the differently doped samples. (b) and (d) show the experimental XANES data of sample C(1.35%) along with calculated spectra for Cu on different sites for the Ga and Cu K-edge, respectively.

Figure 3: Two fitting scenarios of the experimental XANES graph of sample C(1.35%) with different Cu site positions are depicted here. In (a) the Cu_9Ga_4 compound is unstrained while in (b) the lattice constants of Cu_9Ga_4 are subject to 15% strain. The inset in (b) demonstrates the main contribution of the metal compounds to the shape of the measured data.

Figure 4: The measured XLD spectra are depicted. (a) and (b) are the XLD spectra of the Ga K-edge prior to and after etching of the samples, respectively. (c) and (d) show the XLD spectra of the Cu K-edge before and after etching of the samples, respectively.

Figure 5: The intenstity increase of the XLD peaks of the Ga K-edge are shown as a function of the nominal doping concentration.

Figure 6: Comparison of the measured Ga K-edge XLD signal to the simulated ones. (a) shows the undoped spectra, while (b) displays the measured graph of sample C(1.35%) in comparison to calculated spectra for different Cu site possibilities.

Figure 7: Comparison of the XLD signals of strained Cu_9Ga_4 (a) and (c) and the experimental curve (b) of sample C(1.35%) at the Cu K-edge.

Figure 8: Cu K-edge XLD data for the experimental result of sample C(1.35%) (f) and calculated scenarios (a-e), see text for details.

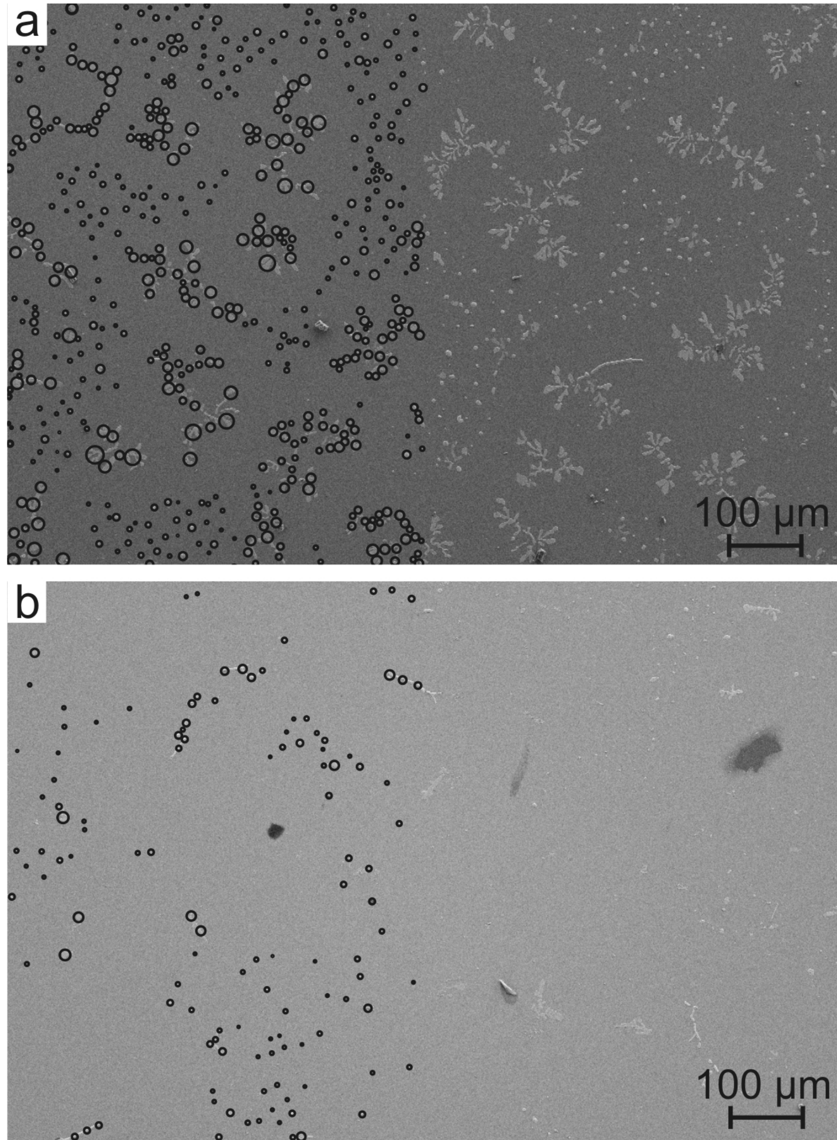
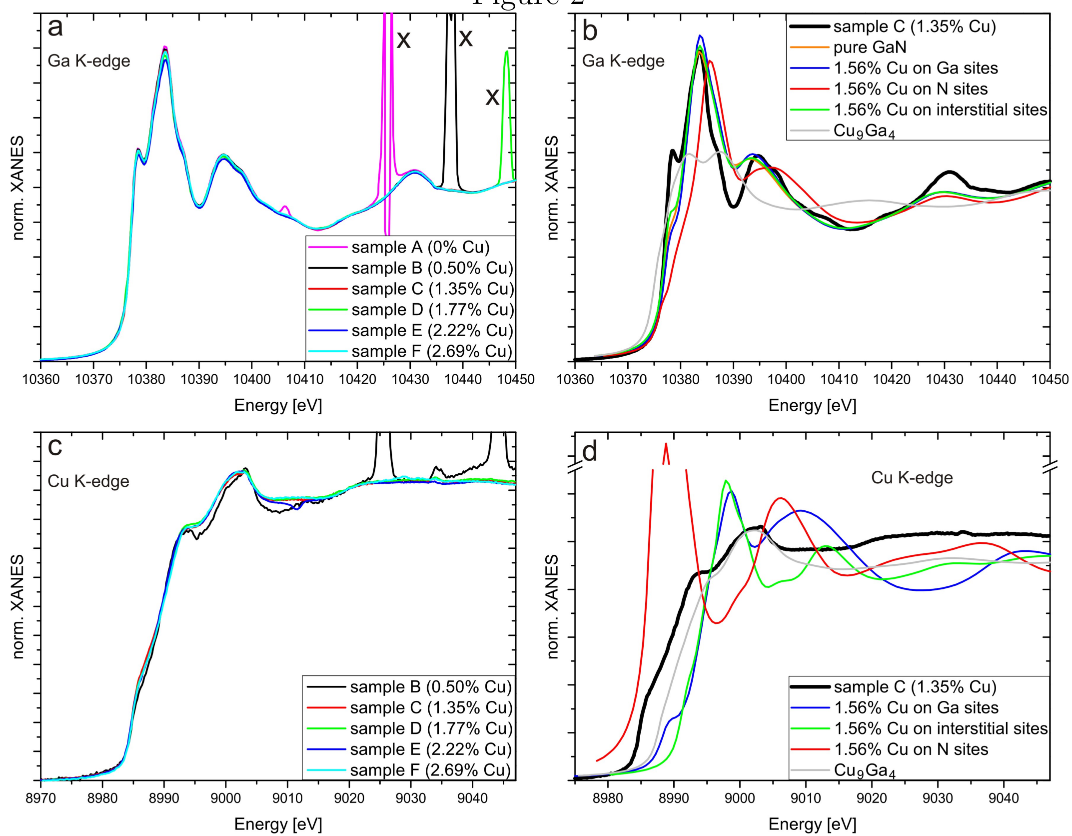


Figure 1

Figure 2



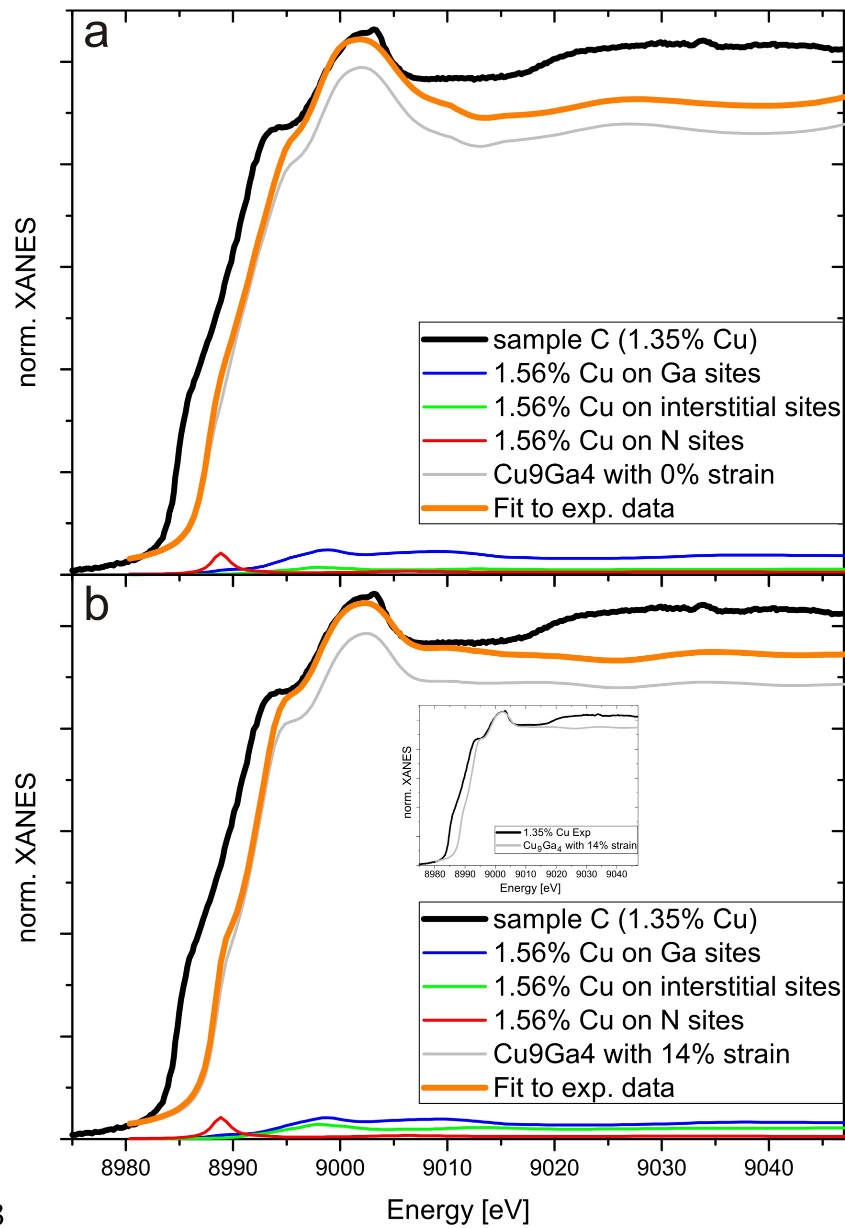
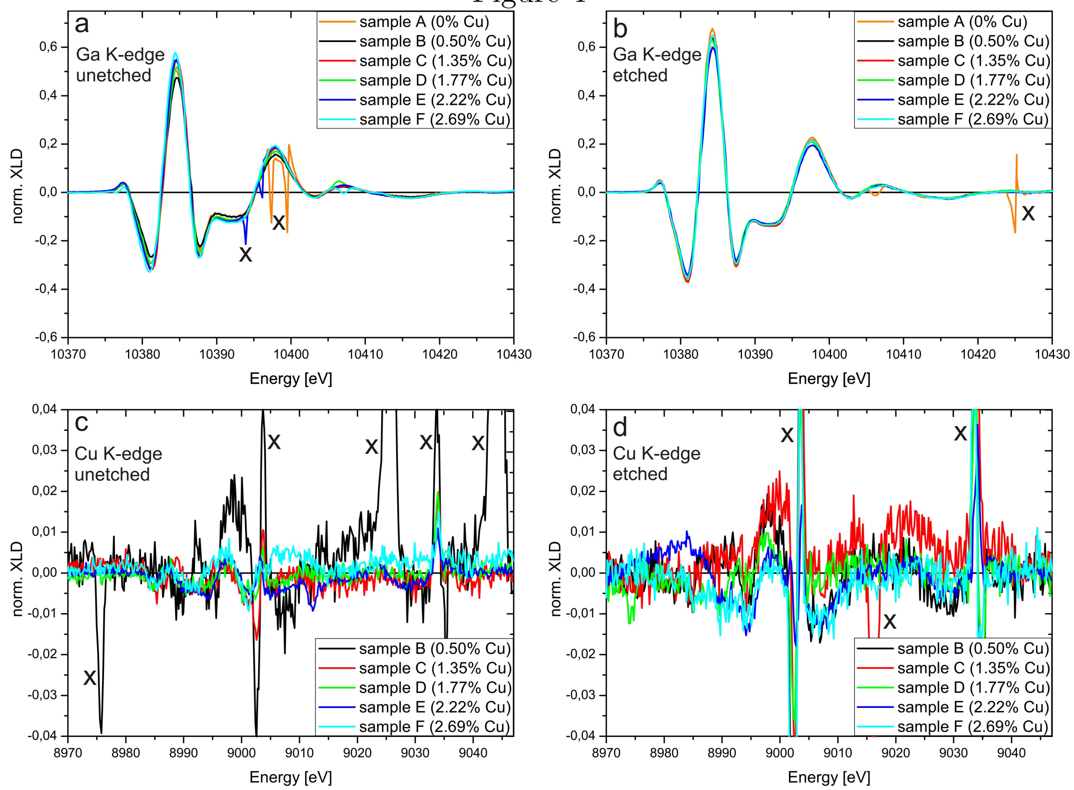


Figure 3

Figure 4



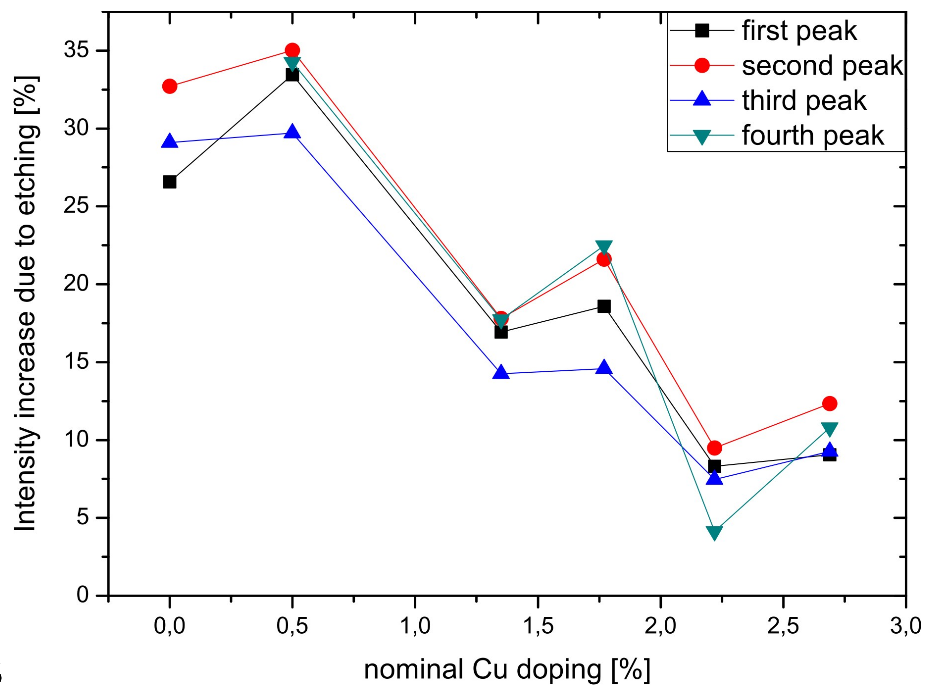


Figure 5

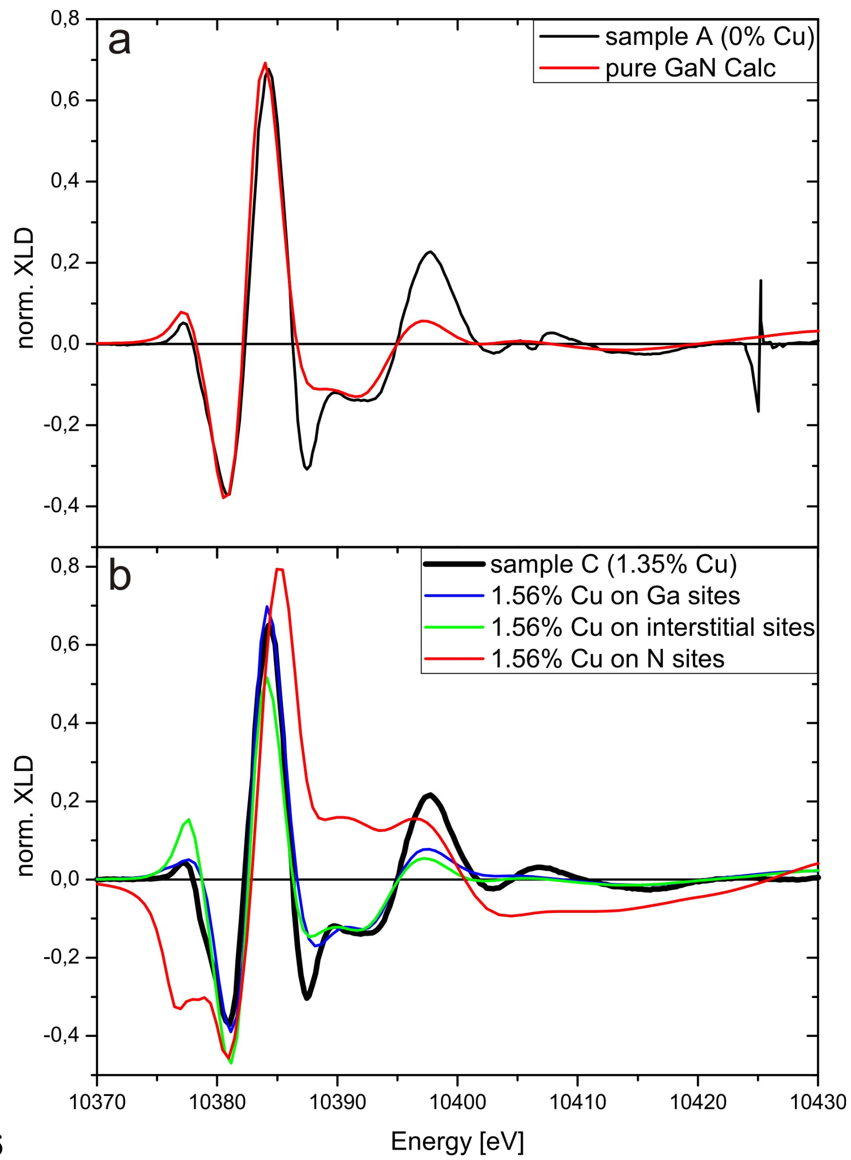


Figure 6

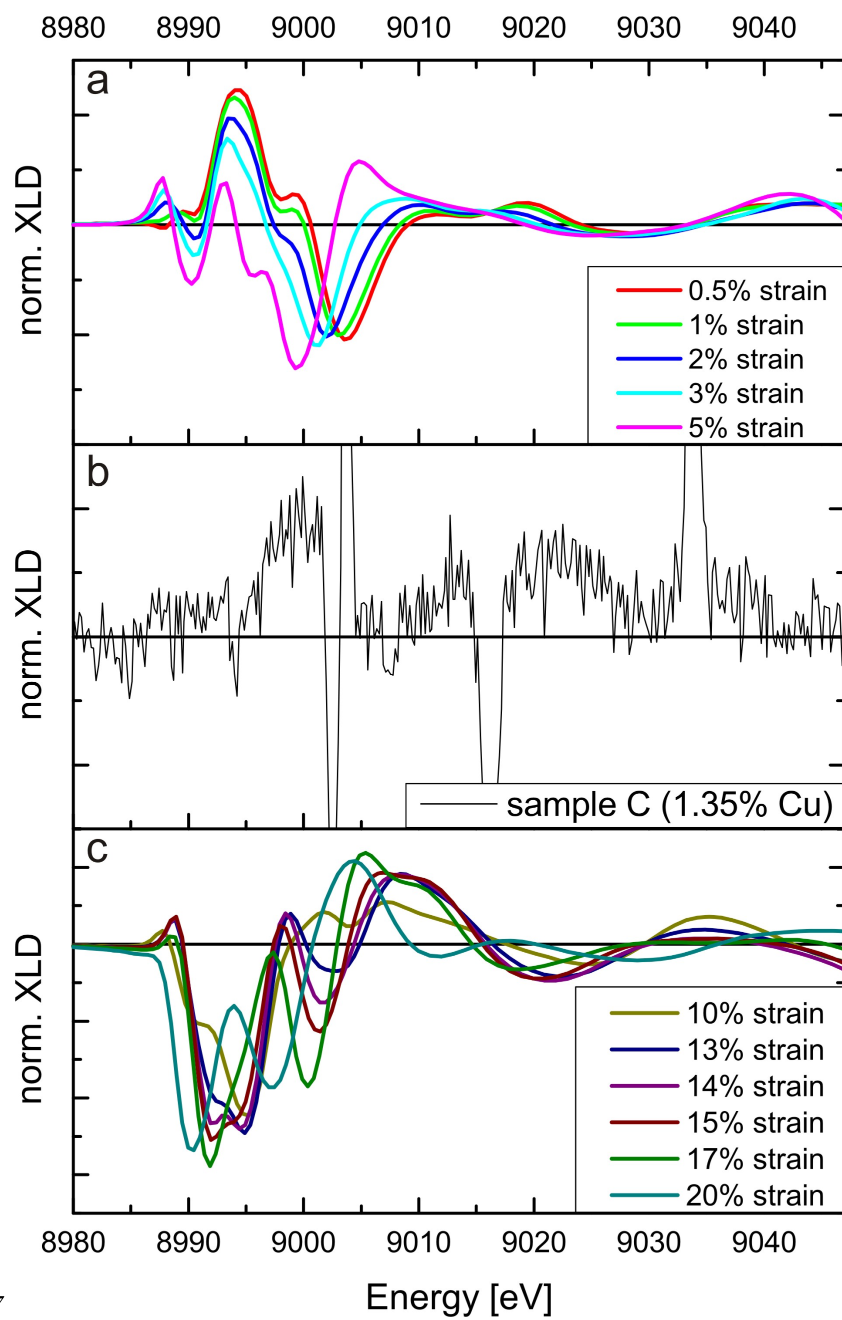


Figure 7

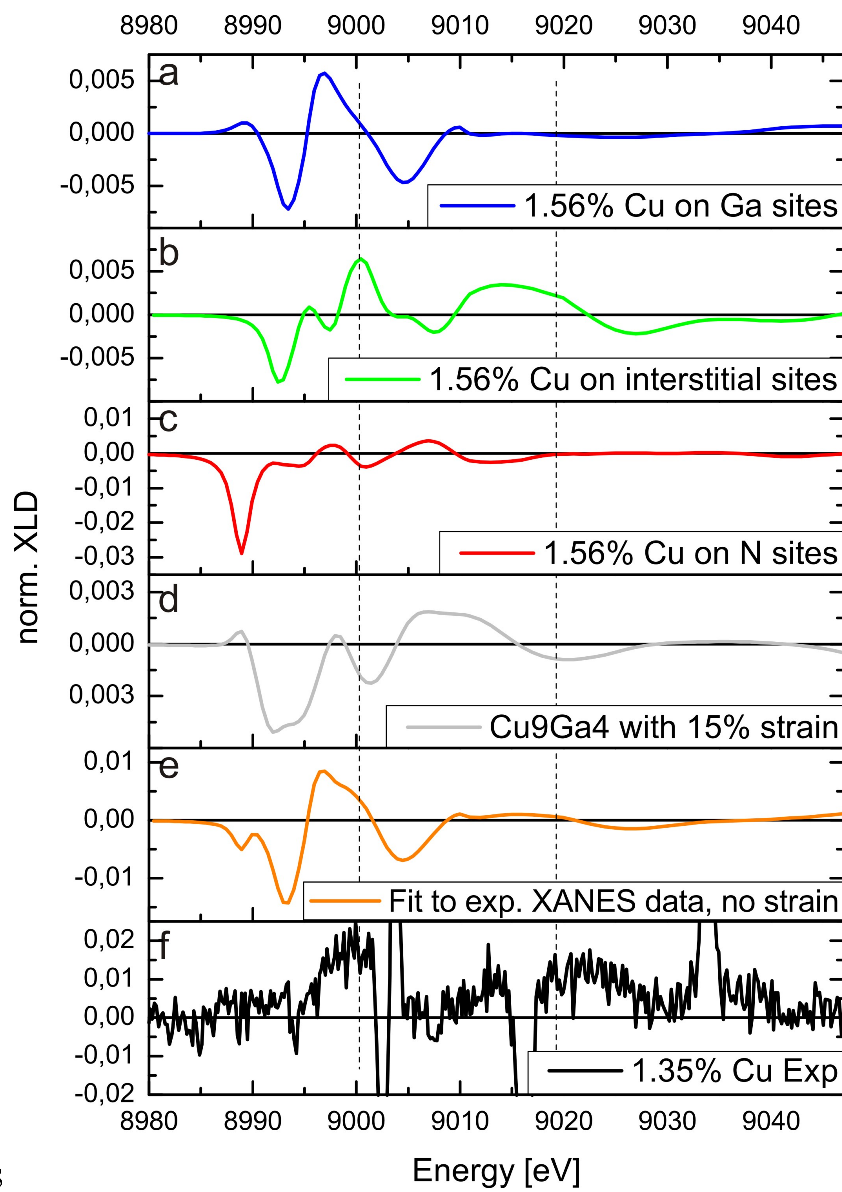


Figure 8