Spectroscopic Identification of the SiO_2 Complex in Oxygen-Implanted GaAs:Si

H. Ch. Alt
Fachhochschule München, Fachbereich Mikrotechnik/Physikalische Technik, Postfach 20 01 13, 80001 München, Germany

H. Müssig* and H. Brugger*
Daimler-Benz AG, Forschungszentrum Ulm, Postfach 23 60, 89013 Ulm, Germany
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Oxygen-implanted and annealed GaAs:Si epitaxial layers have been investigated by low-temperature Fourier transform infrared absorption spectroscopy. Several new local vibrational modes are observed in the range from 614 to 641 cm^{-1}. Isotope shifts and splittings allow the unambiguous chemical identification of the defect involved as SiO_2. A microscopic structure model is developed which provides, based upon a simple fit, the correct vibrational frequencies. Evidence is presented that deep levels associated with this complex are causing the high sheet resistance of the layers. [S0031-9007(97)03789-7]

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In spite of the fact that oxygen was among the earliest impurities to be studied in GaAs, the knowledge of oxygen-related defects in this material is by far not complete. At the beginning of the work on semi-insulating (SI) GaAs in the 1960s, several reports claimed that a high oxygen partial pressure during crystal growth or Ga_2O_3 added to the melt leads to high electrical resistivities of the ingot. However, it is now well established that an intrinsic defect, the EL2 center, is the dominating deep trap in nominally undoped SI GaAs [1]. Different from Czochralski-grown Si or GaP, the total chemical oxygen content in single crystal bulk GaAs usually is rather low, in most cases below 1×10^{16} cm^{-3} [2].

First spectroscopic evidence for isolated oxygen in bulk crystals was based on the observation of a local vibrational mode (LVM) near 840 cm^{-1} in the infrared (IR) absorption spectrum of oxygen-doped GaAs [3]. The assignment as twofold coordinated interstitial oxygen, breaking a Ga-As bond similar to the configuration of interstitial oxygen in Si [4], was confirmed later [5]. Recently, there has been considerable interest in an oxygen-related center exhibiting negative-U behavior [5–9]. This defect occurs in Bridgman- and Czochralski-grown crystals and shows three charge-state dependent LVMs at 731, 715, and 716 cm^{-1} [9–11]. Fine-structure splitting due to the host isotopes ^{69}Ga and ^{71}Ga and piezospectroscopic results [12] are consistent with an off-center substitutional oxygen defect of C_{2v} symmetry (Ga-O_{As}-Ga center), the structural analog of the A center in Si [13].

The situation remained much more unclear concerning the behavior of oxygen implanted into GaAs. Already 20 years ago, Favennec [14] reported on the conversion of conductive n-GaAs layers into SI material after oxygen implantation and thermal annealing. Possible applications in the field of device isolation technologies were the reason for numerous studies devoted to this topic [15] and to the related problem of the influence of oxygen on the electrical characteristics of epitaxially grown GaAs/AlGaAs layers [16]. In pure GaAs, oxygen seems to behave differently from other implanted species such as boron, so that a chemical activity of oxygen in particular in conjunction with Si-doped material was invoked [1,14]. However, no conclusive experimental evidence for a specific oxygen-related electrically active center has been given.

In this Letter a Fourier transform infrared (FTIR) absorption study of Si-doped GaAs layers grown by molecular beam epitaxy (MBE) and implanted with oxygen is presented. After rapid thermal annealing (RTA) high-resistivity behavior of extraordinary thermal stability (up to $\approx$750 °C) can be achieved in these layers [17]. Therefore, MBE regrowth processes at substrate temperatures of >600 °C are possible. One application is a novel technology for the monolithic integration of millimeter wave integrated circuits [18]. In the IR absorption spectrum of the layers, LVMs are detected which show a shift with both the oxygen and silicon isotope mass. This allows, for the first time, the unambiguous chemical identification of a silicon-oxygen complex in GaAs. The defect can be created in concentrations above 10^{18} cm^{-3}, 2 orders of magnitude higher than any other oxygen-containing defect in GaAs reported so far.

Standard starting structures used for the present studies were 750-nm-thick uniformly Si-doped GaAs layers grown by conventional MBE on SI (001)-oriented GaAs substrates. Details are reported elsewhere [17]. The free carrier concentration of 5×10^{18} cm^{-3} from Hall data corresponds to the chemical Si concentration determined by secondary ion mass spectrometry. ^{16}O and ^{18}O implants were carried out using a special ion energy scheme (450, 250, 120, and 40 keV) in order to obtain a uniform oxygen profile of about 3×10^{19} cm^{-3} down to a depth of 750 nm. Thermal annealing was achieved with a RTA

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process using annealing temperatures T_A between 530 °C and 880 °C. Implantations of Si isotopes into undoped MBE layers were used to prepare layers with varying relative concentrations of ^{28}Si and ^{29}Si. The total chemical silicon profile is the same as in the Si-doped MBE layers down to a depth of 650 nm. In this case silicon was electrically activated by RTA prior to the oxygen implantation. Low-temperature FTIR measurements were performed on a high-resolution vacuum instrument (Bruker IFS 113v) equipped with a liquid-nitrogen cooled mercury cadmium telluride detector.

A sequence of typical FTIR spectra taken at 10 K from Si-doped MBE samples implanted with ^{16}O are depicted in Fig. 1. As-implanted samples show a relatively broad band at 843 cm^{-1} which can be assigned to the LVM of interstitial oxygen [3,5]. The broadening and shift from the line position observed in bulk crystals (845 cm^{-1} at 10 K) is probably caused by irradiation damage and associated strain. A weak feature at 731 cm^{-1} being due to off-center substitutional oxygen (O_{As}) [6,7] is observable only for an intermediate RTA temperature of 530 °C. A so-far unreported line is detected at 641 cm^{-1} for T_A between 630 °C and 880 °C. The behavior of this line will be discussed in detail in the following. The line is not observed in reference samples where either undoped MBE layers were used or no oxygen implantation was carried out. The obvious conclusion is that both Si and O must be present. The position and shape of the line do not change significantly up to measurement temperatures of at least 80 K. The width of the line is slightly sample dependent with a minimum of 1.2 cm^{-1} at 10 K.

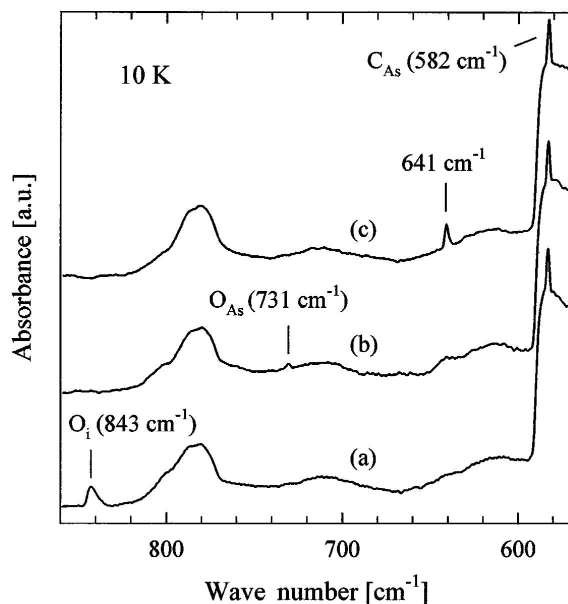

FIG. 1. Low-temperature (10 K) FTIR absorption spectra of ^{16}O-implanted GaAs:Si MBE layers: as-implanted (a), annealed at 530 °C (b), and annealed at 730 °C (c). The LVM at 582 cm^{-1} is due to C_{As} in the substrate.

The influence of the O and the Si isotope masses on the line is shown in Fig. 2. Using ^{18}O as the implant species, the line shifts from 640.8 to 613.8 cm^{-1}. The ratio of the two vibrational frequencies is 1.044. This value should be compared with a pure $1/\sqrt{m}$ dependence giving 1.061, and the experimentally observed shift for the 716-cm^{-1} LVM of the isolated O atom in the Ga-O-Ga center giving 1.053 for this ratio [5]. We conclude that primarily an oxygen vibration is the origin for the 641/614 cm^{-1} line. Further constituents of the underlying defect apparently reduce the O isotope shift. This is verified by the shift with the Si isotope mass: The ^{16}O line shifts from 640.8 to 639.2 cm^{-1} when replacing ^{28}Si by ^{29}Si. Therefore, also silicon must be part of the defect. As the shift is comparatively small (only 14% of the shift deduced from a $1/\sqrt{m}$ dependence), this constituent is not dominating the vibrational state. Using equal doses of ^{28}Si and ^{29}Si, a splitting of the line into two components of nearly equal intensity occurs. This is expected from a defect containing exactly one silicon atom.

After implantation of both isotopes, ^{16}O and ^{18}O, a new doublet evolves at about 630 cm^{-1}. This makes it immediately clear that more than one oxygen atom is involved. A line approximately in the middle between the pure isotope

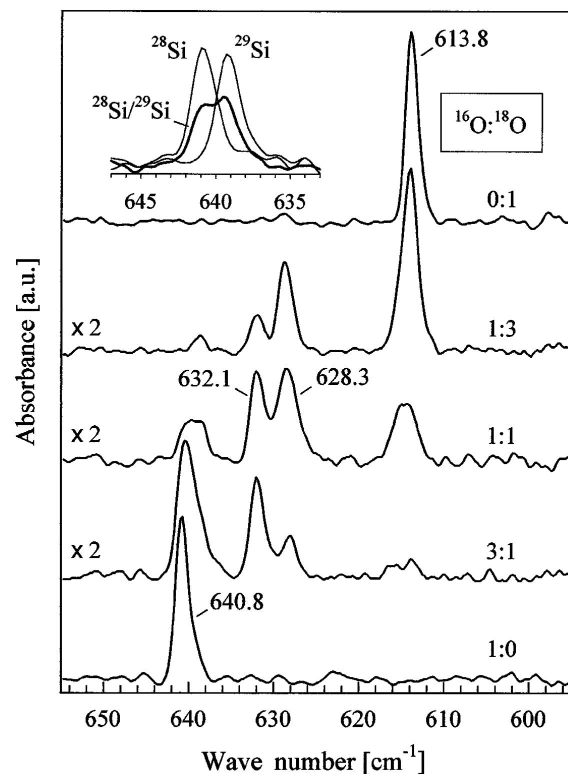

FIG. 2. LVM lines observed in samples implanted with different dose ratios of ^{16}O:^{18}O. Total dose is the same for all samples. The inset shows the isotope shift of the ^{16}O line induced by the silicon isotope mass. All samples were annealed at 780 °C. A smooth background has been subtracted from the original spectra.

lines is expected for a defect containing two equivalent oxygen atoms. This line corresponds to the mixed isotope case where one oxygen atom is ^{16}O and the other ^{18}O. If the two O atoms are slightly inequivalent, the mixed isotope line will split into a doublet, corresponding to the two possible spatial configurations. Further investigations with different dose ratios ^{16}O/^{18}O strongly support this latter model; the integrated absorptions (IA) of the 641-, 630-, and 614-cm^{-1} lines follow closely the statistically expected occurrence of the two isotopes in a X-O_2 center. In the case of a dose ratio of 1:3 (^{16}O:^{18}O), for example, the relative IAs of the three lines are close to 1/16:6/16:9/16. Other models, like a defect containing three O atoms, are not compatible with the experimental data, either with regard to the number or the intensities of the lines. Remarkably, the intensities of the two components of the mixed isotope doublet are not equal, but the high-energy component is roughly proportional to the ^{16}O dose and the low-energy component to the ^{18}O dose, respectively. This behavior could be correlated with the formation kinetics of the defect. The existence of a site-specific precursor state which is linearly dependent on the isotope dose would provide an explanation. It should also be mentioned that, in the case of mixed implantations, the pure ^{16}O and ^{18}O lines show a slight shift and broadening. As this behavior is not reproducible from sample to sample, it is believed that inhomogeneities in the epitaxial layer are the origin. Further investigations are necessary to elucidate these details.

Isotope implantation shows that the core of the complex consists of two oxygen and one silicon atom. It is therefore tempting to construct a microscopic defect model on the basis of an O-Si-O molecule. Considering the incorporation of the defect into the GaAs lattice, it is reasonable to assume that the silicon atom remains on its Ga lattice site. Furthermore, from structural considerations the Si-O bonds should be oriented along the ⟨111⟩ directions. Taking into account the inequivalence of the two oxygen atoms, it is suggested that one oxygen atom is interstitial and the other substitutional. From another point of view, the complex can be described by a pair of the well-known O_i and O_{As} defects bridged by a substitutional Si_{Ga} atom. This microscopic defect model, symmetry type C_s, is shown in Fig. 3. The high Si-O bond energy [19] is considered as the driving force for the thermal stability of the complex and the high concentration attainable (see below).

The high frequencies of the observed LVMs must be due to stretching modes of the O-Si-O molecule. In a first-order approximation it is therefore possible to treat the observed modes as vibrational eigenstates of a linear molecule. Coupling to the GaAs matrix can be performed in the "rigid lattice" approximation by introducing two additional stretching force constants between the oxygen atoms and their neighbors and by using an effective mass $M' = M_{Si} + \Delta M$ [20] for the central silicon atom, taking into account the hindered motion due to the two

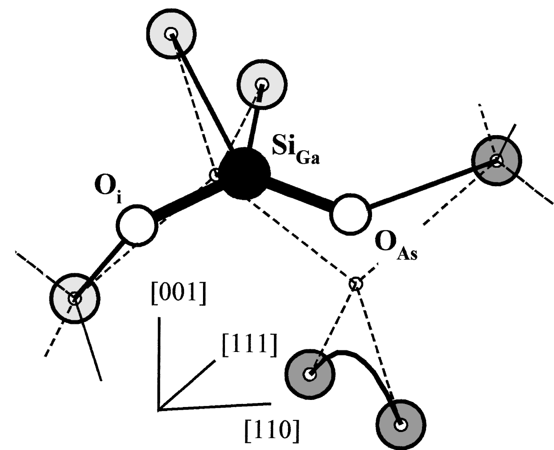

FIG. 3. Structure model of the SiO_2 complex. Ga atoms: dark gray, As atoms: light gray. Si-O bond lengths are adjusted to the nominal value of 0.16 nm [4].

Si-As bonds. Thus four parameters, f(Si-O), f(O_i-As), f(O_{As}-Ga), and ΔM, enter the calculation. Such a model gives three eigenfrequencies corresponding to asymmetric stretching, (quasi-)symmetric stretching, and collective in-phase motion of low frequency. The observed LVMs must be attributed to the asymmetric stretching mode which has the highest frequency. The symmetric stretching shows only a very small shift with the silicon isotope mass. The result of the fit to the experimentally observed line positions is given in Table I. The difference between experiment and calculation is 0.2 cm^{-1} at a maximum. In view of the experimental uncertainty of the line positions of ± 0.1 cm^{-1} this result is satisfactory. The fitted force constants are f(Si-O) = 164 N/m, f(O_i-As) = 146 N/m, and f(O_{As}-Ga) = 132 N/m; the effective mass of ^{28}Si, M' is 39.7 amu; therefore ΔM = 11.7 amu.

The dependence of the sheet resistivity of the MBE layer on the RTA temperature T_A is characterized by two maxima [17]. The first maximum occurs at $T_A \approx 600$ °C and is due to damage-related carrier trapping. For $T_A \geq 600$ °C the conductivity of the layer recovers again along with the reduction of the implantation damage. This is usually observed with standard implantation techniques for device isolation in GaAs [15]. The second maximum

TABLE I. Comparison between experimentally observed and calculated LVM frequencies (cm^{-1}) of the SiO_2 defect molecule under different isotopic substitutions. The calculations are for the asymmetric stretching of a linear O-Si-O molecule embedded into a rigid GaAs matrix.

Molecule type	Experiment	Calculation
$^{16}O_i$-$^{28}Si_{Ga}$-$^{16}O_{As}$	640.8	641.0
$^{16}O_i$-$^{29}Si_{Ga}$-$^{16}O_{As}$	639.2	639.1
$^{18}O_i$-$^{28}Si_{Ga}$-$^{18}O_{As}$	613.8	613.8
$^{18}O_i$-$^{28}Si_{Ga}$-$^{16}O_{As}$	632.1	632.0
$^{16}O_i$-$^{28}Si_{Ga}$-$^{18}O_{As}$	628.3	628.2

at $T_A \approx 750\,^\circ\mathrm{C}$ is found only in oxygen-implanted layers and must be attributed to a chemical effect of oxygen. If the SiO_2 complex is responsible for the high-resistivity behavior of the O-implanted MBE layer, its concentration must be of the order of magnitude of the Si_{Ga} doping concentration.

The IA of a LVM (in cm^{-2}) is directly proportional to the concentration of the center involved [20]. Thus the Si_{Ga} concentration can also be measured by FTIR using the calibration factor (proportionality factor) of $5 \times 10^{16}\ cm^{-1}$ for the 384-cm^{-1} LVM [21]. The IA measured in the as-grown MBE layer corresponds to a Si_{Ga} concentration of $5.5 \times 10^{18}\ cm^{-3}$, in good agreement with the free carrier concentration determined from Hall data. No Si_{Ga} LVM can be detected for $T_A \geq 700\,^\circ\mathrm{C}$. On the other hand, in the temperature range between 730 °C and 830 °C, the 641-cm^{-1} line has within $\pm 20\%$ the same IA as the Si_{Ga} LVM in the as-grown layer. Even if the calibration factor of the new line is not yet known, a reasonable estimate gives that it is also in the 10^{16}-cm^{-1} range [22]. This implies that the defect concentration is between 10^{18} and $10^{19}\ cm^{-3}$. Furthermore, from the complete disappearance of the Si_{Ga} LVM and the fact that no other new LVMs were detected in the spectral range 200–850 cm^{-1} it is concluded that the SiO_2 complex consumes essentially all available silicon in the layer. It is therefore suggested that the defect determines the electrical behavior of this layer.

Further work on the electrical activity of the SiO_2 complex remains to be done in the future. However, the model presented gives at least an intuitive picture for the removal of the shallow donor (Si_{Ga}) electrons. It is known that off-center substitutional oxygen O_{As} forms a negative-U center which binds, in the acceptorlike state, a second electron with ≈ 0.7 eV [10,11]. Interstitial oxygen O_i, on the other hand, is electrically inactive by analogy to oxygen in silicon [4]. In comparison with the two isolated oxygen defects, the SiO_2 complex has one additional valence electron, the donor electron of Si_{Ga}. This electron can now be bound deeply by the neighboring O_{As} center.

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*Present address: United Monolithic Semiconductors (UMS) GmbH, Wilhelm-Runge-Strasse 11, 89081 Ulm, Germany.

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