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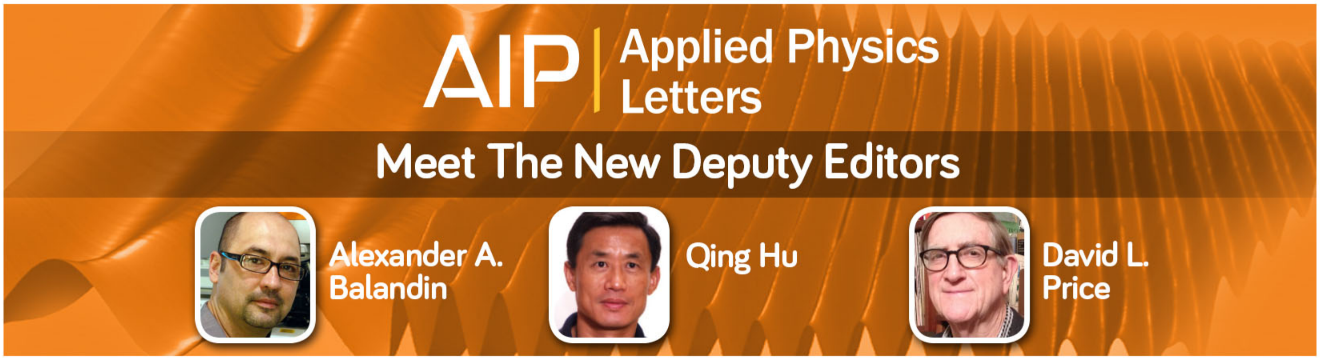

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Electrical conductivity and carrier concentration control in β-Ga_2O_3 by Si doping

Encarnación G. Víllora,[1,a)] Kiyoshi Shimamura,[1] Yukio Yoshikawa,[2] Takekazu Ujiie,[2] and Kazuo Aoki[2]
[1]*National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan*
[2]*Koha Co., Ltd., 2-6-8 Kouyama, Nerima-ku, Tokyo 176-0022, Japan*

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Electrical conductivity of β-Ga_2O_3 has been attributed so far to an oxygen deficiency, the donors presumably being oxygen vacancies. This letter shows, however, that the conductivity can be intentionally controlled over three orders of magnitude by Si doping. The related free-carrier concentration, which varies between $10^{16}-10^{18}$ cm^{-3}, corresponds to a 25%–50% effective Si donors. Since Si is the main impurity present in Ga_2O_3 powders—in the order of the studied doping levels—we conclude that the electrical conductance of β-Ga_2O_3 can be attributed to Si impurities, and that the contribution of oxygen vacancies, if any, is not dominant. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2919728]

β-Ga_2O_3 belongs to the group of the transparent conductive oxides (TCOs). In contrast to standard TCOs (In_2O_3, SnO_2, or ZnO), which are opaque in the uv wavelength region, it exhibits a unique uv transparency with the cutoff at about 260 nm (E_g=4.8 eV[1,2]). β-Ga_2O_3 has been proposed as a substrate for the growth of Ga nitrides since it compromises the transparency of sapphire with the electrical conductivity of SiC; both substrates are commercially used for Ga nitride-based devices. In spite of the difference in crystal structure between β-Ga_2O_3 and GaN, the epitaxial growth of GaN on nitridized β-Ga_2O_3 substrates was demonstrated.[3,4] The production of β-Ga_2O_3 wafers was achieved,[5] but the intentional control of the electrical properties is still a remaining issue for the use of these for different optoelectronic devices.

The electrical properties of β-Ga_2O_3 have been reported by several authors.[6–11] The n-type conductivity of β-Ga_2O_3 has been attributed so far to an oxygen deficiency, which leads to oxygen vacancies or Ga interstitials, i.e., Schottky or Frenkel disorders, respectively. This deviation from the stoichiometry, which is induced by the decomposition of the starting raw material, is a typical feature of TCOs,[12] and by analogy, the most common assumption is the presence of oxygen vacancies. The activation energy of the reaction $Ga_2O_3 \rightarrow GaO + O_2$ is reported to be 492 kJ/mol.[13] There is no evidence of β-Ga_2O_3 evaporation under 1623 K and an oxygen pressure >1 Pa,[14] which is contrary to older reports.[15] In order to preserve the electroneutrality of a crystal, an oxygen vacancy captures two electrons and is denoted as a neutral vacancy $V_O{}^x$ or a color center (F center). Free carriers originate then by single or double ionization, $V_O^{\cdot}$ or $V_O^{\cdot\cdot}$, respectively. The donor-state energy levels are experimentally determined to be located at $E_d \sim 0.02-0.03$ eV below the bottom of the conduction band.[6] Further, by means of electron paramagnetic resonance (EPR), it has been suggested that among the three oxygen sites, only the one in fourfold coordination acts as a vacancy-donor trapping a single unpaired electron,[11] namely $V_O^{\cdot}$.

An increased conductivity of Zr-doped crystals with respect to the undoped one was reported,[7] however, this is much lower than in other reports,[16] and the authors warn themselves that the dopant incorporation is in the order of impurity concentration. In this letter, we show that Si is an effective n-type dopant for β-Ga_2O_3, and that the electrical conduction and free-carrier concentration can be intentionally controlled over three orders of magnitude by Si doping. Si is the main impurity present in Ga_2O_3 powders, and therefore, the common assumption for an impurity band conduction constituted only by oxygen-vacancy donors is not sustainable, at least, in the considered conduction range. The influence of Si doping on the optical properties is reported in a separate paper.[17]

Single crystals were grown by the floating zone technique. The feed rods were prepared by a sintering process, in which a 6N pure or a SiO_2-mixed Ga_2O_3 powder was pressed at room temperature and subsequently annealed under air. In the following, unless otherwise noted, Si concentration (Si_{con}) refers to the nominal Si/Ga ratio. The crystals were grown under a 500 ml/min gas-flow rate and a 5 mm/h pulling speed. The atmosphere was oxidative in order to suppress the evaporation from the molten zone.

The Si_{con} in the doped crystals was determined by inductively coupled plasma (ICP) atomic emission spectrometry. For it, an IRIS Advantage from Nippon Jarrell–Ash Co., Ltd. was utilized. The electrical resistivity and Hall measurements were carried out by the van der Pauw method with an Accent HL5500PC. A magnetic field of 0.33 T was applied. The measurements were done under dark conditions to avoid photogeneration of carriers.

The electrical conductivity is shown as a function of the Si_{con} in the double logarithmic plot of Fig. 1. The conductivity continuously increases by over three orders of magnitude, from a value as low as 0.03 Ω^{-1} cm^{-1} for 6N-purity crystals to 50 Ω^{-1} cm^{-1} for crystals with a high Si_{con}. The Si incorporation saturates at about 0.2 mol % when second-phase segregation appears. The electrical properties and the segregation behavior slightly vary during the growth, since the conditions for a stable molten zone vary with the diameter and length of the growing crystal. Consequently, some fluc-

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[a)] Electronic mail: villora.garcia@nims.go.jp.

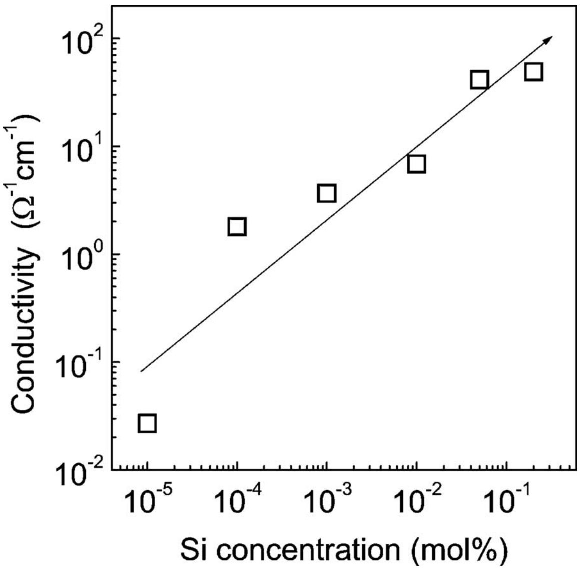

FIG. 1. Electrical conductivity as a function of the nominal Si_{con}. The arrow indicates a systematical increase.

tuation is observed and the given values are to be taken as a reference for any kind of growth technique.

The electrical conductivity σ depends on the carrier concentration n and the mobility μ as $\sigma = en\mu$, where e represents the electron charge. By using Hall measurements, it was found that while the mobility fluctuates around the typical value of 100 $cm^2 V^{-1} s^{-1}$,[18] the free-carrier concentration systematically increases with the Si_{con} by over three orders of magnitude, 10^{16}–10^{18} cm^{-3}, as shown in Fig. 2. Therefore, Si incorporates into β-Ga_2O_3 as a donor without any remarkable change in the mobility of free carriers.

The Si_{con} detected by ICP (Si_{ICP}) versus Si_{con} ($Si_{nominal}$) is displayed in Fig. 3. The experimental values are fitted by a power-law, $Si_{ICP} = 4 \times 10^{10}\ Si_{nominal}^{0.41}$, which indicates that the Si_{con} does not linearly scale up with the nominal doping concentration. At low-doping levels, Si remains in the crystal, while at high-doping levels, the concentration drops to about 5% of the nominal one. The origin for this functional dependence is not clear at present—it can even not be extrapolated to nominal doping concentrations below 10^{18} cm^{-3}—, and it could be a confluence of diverse factors such as the difference in partial vapor pressure, chemical reactions, etc. If we compare now the carrier concentration n with the concentration of Si (Si_{ICP}), we find that n systematically increases with Si_{ICP}, and that for each concentration, the percentage of Si atoms that act as donors varies between 25% and 50%. This observation can be interpreted by previous EPR studies,[11] if we assume that Si^{4+} evenly substitutes Ga^{3+} in the two cationic sites, Ga_4 and Ga_6 (four- and sixfold coordination, respectively). According to EPR, the donors are located in a fourfold symmetric site, and therefore, only 1/2 of the Si atoms (Si_{Ga_4}) are potential donors.

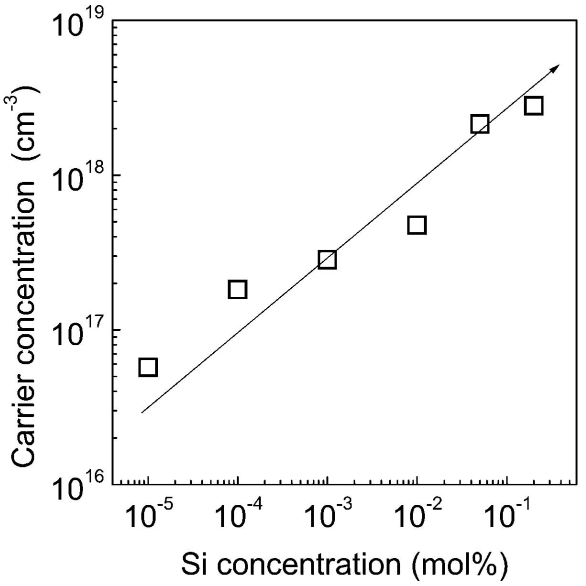

FIG. 2. Free-carrier concentration as a function of the nominal Si_{con}. The arrow indicates a systematical increase.

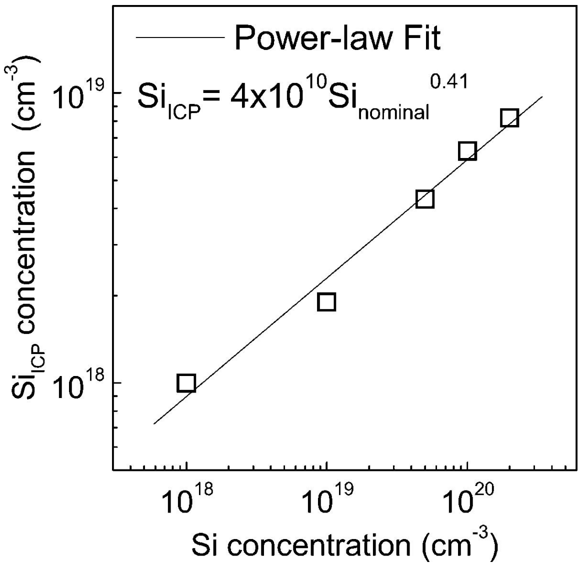

FIG. 3. Measured Si_{con} (Si_{ICP}) vs nominal ($Si_{nominal}$).

If we now consider that Si is the main impurity found in Ga_2O_3 powders, depending on the batch and maker, the given purity varies between 10–20 ppmwt for 4N and 0.05–1.8 ppmwt for 6N powders. These values correspond to a Si concentration in the order of $(1-3) \times 10^{18}$ cm^{-3} and 10^{16}–10^{17} cm^{-3}, respectively. Comparing these values with the ones of intentional doping given above, it is seen that commercially available Ga_2O_3 powders can be considered as effectively Si doped. In the investigated doping range, the phenomenon of electrical conduction can be linked to Si doping, and the attribution to ionized oxygen vacancies is no longer sustainable. However, the possibility for a contribution of oxygen vacancies to the electrical conduction is not excluded. In order to clarify this point, higher purity Ga_2O_3 raw materials should be produced.

At this stage, we want to examine possible candidates for n-type doping. Table I shows the atomic radii of Ga^{3+}

TABLE I. Atomic radii R of Ga and some elements of the group 3B in four and sixfold coordination.

Atom	Valence	R_4 (pm)	R_6 (pm)	Average $\Delta R/R_{Ga}$ (%)
Ga	3+	47	62	⋯
Si	4+	26	40	−40
Ge	4+	39	53	−16
Sn	4+	55	69	+14

TABLE II. Partial vapor pressures of the species obtained from oxidized forms of the elements in Table I.

System	Species	T (K)	P (atm)	Reference[a]
Ga–O	Ga	2068	$4.2 \pm 0.8 \times 10^{-5}$	20
	Ga	2068	1.9048×10^{-4}	14
	Ga_2O	2068	$4.5 \pm 0.9 \times 10^{-4}$	20
	Ga_2O	2068	1.3718×10^{-2}	14
	GaO	2068	$4.0 \pm 0.8 \times 10^{-6}$	20
	Gao	2068	1.885×10^{-5}	14
	O	2068	$2.8 \pm 0.8 \times 10^{-5}$	20
	O	2068	1.717×10^{-5}	14
Si–O	SiO_2	2068	0.782×10^{-6}	22
	SiO	1685	0.897×10^{-2}	22
Ge–O	GeO_2	1993	0.529	22
	GeO	982	1.00	22
Sn–O	SnO_2	1893[b]	0.114×10^{-1}	22
	SnO	2068	0.806	22

[a] Given values are only a comparative reference due to a strong dependence on the surrounding atmosphere (Refs. 14 and 21).

[b] $SnO_2 \rightarrow SnO + O_2$ sublimates at the melting point $T_m = 1893$ K.

together with those of Si^{4+}, Ge^{4+}, and Sn^{4+} in four- and sixfold coordination. Si^{4+} and Ge^{4+} have a smaller radius than Ga^{3+}, while Sn^{4+} has a larger one. From the point of view of atomic radius, Ge^{4+} and Sn^{4+} fit better than Si^{4+} in the Ga^{3+} cationic site. It is necessary, however, to compare the partial vapor pressures of the different species, which are summarized in Table II. There is no evidence for the existence of Ga_2O_3 molecules in the gas phase, and Ga_2O and GaO are thermodynamically unstable in the solid state.[19] At the melting point ($T_m = 2068$ K), β-Ga_2O_3 evaporates in the reduced form Ga_2O, the partial vapor pressure being estimated to be 0.014 atm,[14] or experimentally to 4.5×10^{-4} atm.[20] (Although these values are in apparent contradiction, it should be noticed that even small variations in composition can cause a large change in the equilibrium state.[14,21]). The vapor pressures of the species from the Ge–O and Sn–O systems are close to 1 atm even at temperatures below the β-Ga_2O_3 melting temperature. Instead, the vapor pressure of SiO_2 is lower than that of the species in the Ga–O system, and the more reduced form of SiO has a comparable one. Therefore, for any growth technique from the β-Ga_2O_3 melt, Si remains in the melt, while Ge and Sn evaporate to a high extent. We can conclude that although Ge or Sn can accommodate better in the β-Ga_2O_3 lattice, Si has a higher potential as an n-type dopant for crystals grown from the melt, since it is the only one whose concentration can be intentionally controlled.

Summarizing, presented results evidence that the electrical conductivity in β-Ga_2O_3 can be intentionally controlled over three orders of magnitude by an increase in the free-carrier concentration with Si doping. The previous attribution to oxygen vacancies is questioned, since Si is found to be the main impurity in correlative concentrations. A wider control range is expected when higher-purity raw materials are available. Si^{4+} is an effective n-type dopant when substituting Ga^{3+} atoms in fourfold coordination. Other doping candidates such as Ge^{4+} or Sn^{4+} are not feasible for growth techniques from the melt, since the vapor pressures of GeO_2 and SnO_2 are very high at the β-Ga_2O_3 melting point.

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