



# Control and understanding of metal contacts to $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals: a review

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## Abstract

Gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) is a promising semiconductor for high power devices and solar blind ultraviolet photodetectors due to its large bandgap, a high breakdown field, and high thermal stability. Recently, a considerable achievement has been obtained for the growth of high-quality  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and high performance  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based devices. However, rapid advance in device performance can be limited by the critical issues of metal contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> such as barrier height, leakage current, ohmic contact, and surface, interfacial and deep states. This article aims to provide a review on the recent studies in the control and understanding of metal contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, particularly in terms of the barrier formation. This review suggests that understanding the current transport mechanisms of metal contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> more thoroughly is necessary to enhance the performance, stability and reliability of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based devices.

**Keywords** Gallium oxide · Metal contacts · Barrier formation · Current transport mechanisms

## 1 Introduction

As an emerging semiconductor,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has attracted significant interest as next-generation high-power devices due to its wide bandgap (~4.85 eV) and theoretical critical field strength of 8 MV/cm [1]. High-performance power devices have been demonstrated in the form of Schottky barrier diodes [2–4] and field effect transistors (FETs) [5–7]. Enhancing the device performance further as theoretically predicted requires high-quality epitaxial layer with low compensating defects and low background doping. In addition,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has been applied to other devices such as solar blind ultraviolet photodetectors [8], electroluminescent devices [9], window materials for optoelectronic devices [10], transparent conductive oxides [11], and hydrogen gas sensors [12].

Because of the highly asymmetric monoclinic crystal structure,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has known to have anisotropic material

properties. Guo et al. found that thermal conductivity along the [010] direction is approximately three times larger than along the [100] direction [13]. Anisotropic nonlinear optical properties in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> have been reported [14, 15]. Liu et al. grew  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> epilayers on *r*- and *c*-plane sapphire substrates and showed that  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> epilayers on *r*-plane revealed higher UV responsivity and detectivity [16]. Wong et al. reported an electron mobility anisotropy in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> FETs, associated with the anisotropic carrier scattering [17]. Zhang et al. investigated the anisotropic etching behavior of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and showed that the wet etching in hot phosphoric acid could effectively reduce the sidewall roughness caused by plasma dry etching [18]. Jang et al. found that ( $\bar{2}$  01) Ga<sub>2</sub>O<sub>3</sub> had higher etch rates and could form ohmic contacts more easily than (010) Ga<sub>2</sub>O<sub>3</sub>, which was correlated with the higher density of oxygen dangling bonds on the ( $\bar{2}$  01) plane [19]. Sasaki et al. found that the epitaxial growth rate for (100) plane

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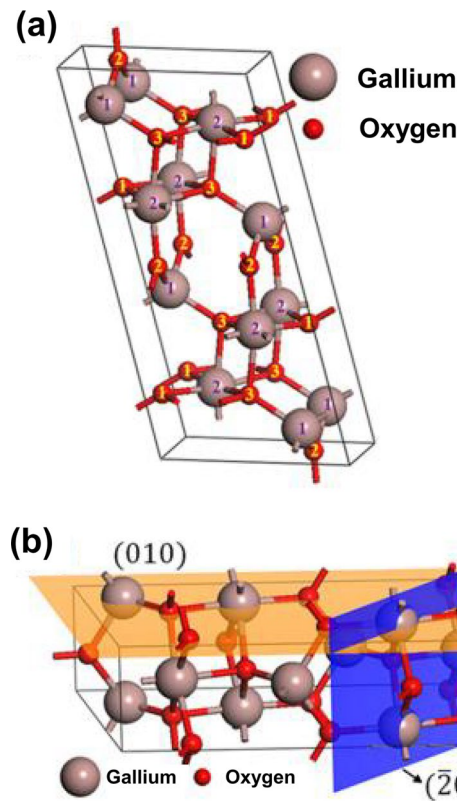


was lower than (010) plane because of the low adhesion energy on the terraces for (100) surface [20]. Fu et al. comparatively investigated Schottky contact to  $(\bar{2}01)$  and (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> interfaces and found higher barrier height, lower reverse leakage current, and larger breakdown voltage for (010) orientation [21]. Bhattacharyya et al. fabricated Schottky contacts to (010),  $(\bar{2}01)$  and (100)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrates and found that the barrier heights for (010) orientation are highest among three orientations [22]. These anisotropic material properties definitely give a significant impact on the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based device performance.

Metal–semiconductor (MS) Schottky contacts are utilized to investigate the nature of defects and their impact on the material quality and the electrical characteristics. MS contacts are classified into two categories, namely, Schottky and ohmic contacts. The barrier height in a metal contact to an n-type semiconductor is given by  $\Phi_B = \Phi_M - \chi$ , where  $\Phi_M$  and  $\chi$  are the metal work function and the electron affinity of the semiconductor (4.0 eV for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [1]), respectively [23]. The work functions for various metals are available in Ref. [24]. Electrical properties of metal/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> contacts according to the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystal orientation have been investigated. For example, Yao et al. investigated the Schottky metal dependent electrical properties of Schottky diodes on  $(\bar{2}01)$  and (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [25]. Schottky barrier heights from current–voltage ( $I$ – $V$ ) and capacitance–voltage ( $C$ – $V$ ) methods of the five metals revealed little dependence on the metal work function. Lyle et al. fabricated Ti contacts on (010) and (001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and observed higher barrier height for (010) plane [26]. Further research on MS contacts can enhance the performance of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-based devices. In this paper, recent studies on the control and understanding of metal contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals has been reviewed.

## 2 Material properties of $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

Among different crystalline phases of Ga<sub>2</sub>O<sub>3</sub>, the monoclinic phase  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has the best thermal stability, while other four phases ( $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>) are metastable and can be transformed to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> at high temperatures [1]. Hence, most studies are focused on  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. Figure 1a shows a schematic draw of the unit cell of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and Fig. 1b shows the (010) and  $(\bar{2}01)$  planes which are most commonly used for device applications [19]. Table 1 summarizes the material characteristics of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, GaN, 4H-SiC, diamond and Si. Except diamond, the bandgap and breakdown field of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> are larger than other semiconductors. The Baliga's figure of merit (BFOM) for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is larger than GaN and 4H-SiC, highly beneficial to fabricate high-power electronic devices. However, relatively



**Fig. 1** **a**  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystal structure and **b** (010) and  $(\bar{2}01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> surfaces [19]

low thermal conductivity can cause self-heating effects. Excessive heat accumulation will degrade the performance and stability of the devices. Relatively low mobility also has a negative effect on the device characteristics.

Bulk Ga<sub>2</sub>O<sub>3</sub> single crystals can be grown using the following methods: edge-defined film-fed growth (EFG) [27], Czochralski (CZ) [28, 29], Floating zone (FZ) [30] and vertical Bridgman (VB) [31]. Using the EFG method, Kuramata et al. [27] obtained a large and high-quality  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals up to 4 inches, with no twin boundaries and the dislocation density of  $\sim 10^3$  cm<sup>-2</sup>. Galazka et al. reported a two-inch-diameter cylindrical  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystal grown by CZ method [29]. FZ method is utilized to grow  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> rod with a typical growth rate of 6 mm/h and a diameter of 10 mm [30]. VB method provides some advantage such that  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals are easily released after growth. Using VB method, Hoshigawa et al. obtained a 25-mm-diameter  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystal [31]. Among these methods, the EFG method is considered to be the most promising technique to grow bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, because of the capability of achieving large size and high quality bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> for future high-volume production [32, 33]. Unintentionally doped (UID) n-type  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals are normally obtained due to the incorporation of Si and

**Table 1** Material properties of  $\beta\text{-Ga}_2\text{O}_3$  in comparison with those of GaN, 4H-SiC, Diamond and Si (Baliga's figure of merit: BFOM) [1]

Properties	GaN	4H-SiC	Diamond	$\beta\text{-Ga}_2\text{O}_3$	Si
Bandgap, $E_g$ (eV)	3.4	3.25	5.5	4.85	1.1
$E_c$ (MV/cm)	3.3	2.5	10	8	0.3
Dielectric constant, $\epsilon$	9.0	9.7	5.5	10	11.8
Electron mobility, $\mu$ ( $\text{cm}^2/\text{V}\cdot\text{s}$ )	1250	1000	2000	300	1480
BFOM ( $\epsilon\mu E_c^3$ ) relative to Si	846	317	24,660	3214	1
Saturation velocity ( $10^7$ cm/s)	2.5	2	1	1.8~2	1
Thermal conductivity ( $\text{W}/\text{cm}\cdot\text{K}$ )	2.3	3.8	20	0.1~0.3	1.5

Ir atoms from the  $\beta\text{-Ga}_2\text{O}_3$  seed and crucible. Hence semi-insulating crystals are achieved by Mg or Fe doping acting as deep acceptors [32, 33].

Low-resistivity  $\beta\text{-Ga}_2\text{O}_3$  substrates can be obtained by intentional doping, which are necessary to achieve better ohmic contacts and lower threshold voltages. For n-type dopants, Sn, Si, and Nb have been employed. Ohira et al. investigated the effect of the annealing process at  $1100^\circ\text{C}$  on the material properties of Sn-doped  $\beta\text{-Ga}_2\text{O}_3$  grown by the FZ method and found that their properties changed marginally [34]. Zhang et al. studied the effect of Sn doping in FZ-grown  $\beta\text{-Ga}_2\text{O}_3$  crystals and reported an increase in the absorption coefficient with the Sn doping and a reduction in the absorption coefficient after annealing, associated with the decrease of free carriers [30]. Víllora et al. obtained Si-doped  $\beta\text{-Ga}_2\text{O}_3$  grown by the FZ method with the Si concentrations of  $10^{16}\sim 10^{18}\text{ cm}^{-3}$  and showed that the conductivity can be intentionally controlled over three orders of magnitude by Si doping [35]. Based on the result, they suggested that electrical conductance of  $\beta\text{-Ga}_2\text{O}_3$  is mainly governed by Si impurities and the contribution of oxygen vacancies, if any, is not significant. Zhou et al. grew Nb-doped  $\beta\text{-Ga}_2\text{O}_3$  by the FZ method and could achieve the carrier concentration from  $9.55\times 10^{16}$  to  $1.8\times 10^{19}\text{ cm}^{-3}$  [36]. In the case of p-type doping, Mg has been used as a dopant. Onuma et al. grew Mg-doped  $\beta\text{-Ga}_2\text{O}_3$  crystals by the FZ method and observed the semi-insulating behavior for Mg concentration of  $4\times 10^{18}$ – $2\times 10^{19}\text{ cm}^{-3}$  [37]. Based on the first-principles calculations, Dong et al. showed that N serves as a deep acceptor with an energy level of 1.33 eV above the valence band maximum, which is not effective as a p-type dopant [38]. Hence the achievement of p-type doped  $\beta\text{-Ga}_2\text{O}_3$  remains a big challenge.

### 3 Schottky barrier diodes

Schottky barrier diodes can be electrically characterized using  $I$ - $V$  and  $C$ - $V$  methods to obtain Schottky barrier heights (SBHs). Assuming the thermionic emission (TE)

model, the forward bias  $I$ - $V$  characteristics of a Schottky diode are analyzed using the following equation [23]

$$J = A^{**} T^2 \exp(-q\phi_B/kT) [\exp\{q(V - IR_S)/nkT\} - 1] \quad (1)$$

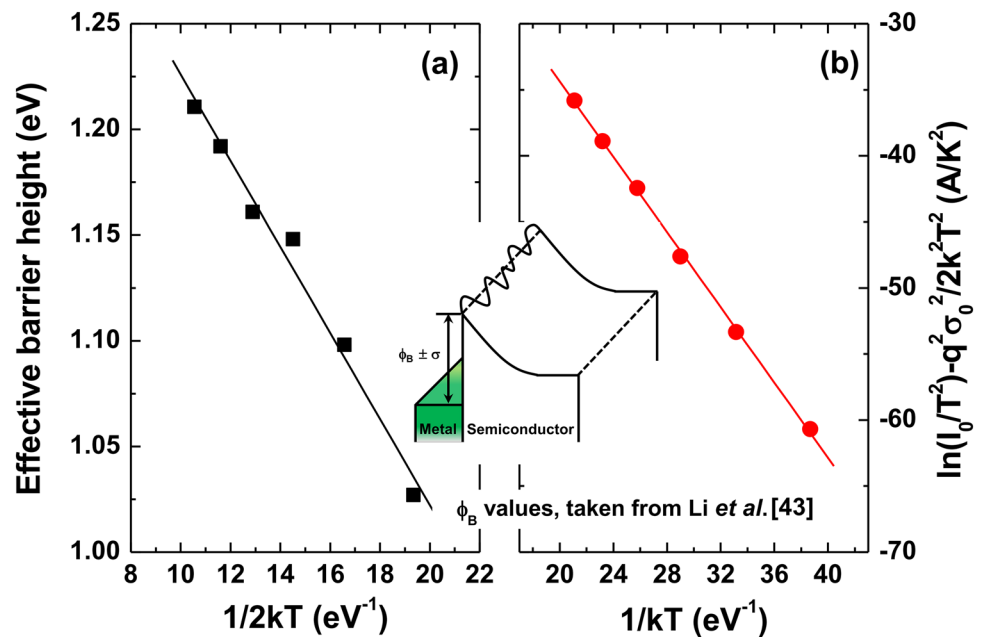
where  $A^{**}$  is the effective Richardson constant ( $41.1\text{ cm}^{-2}\text{ K}^{-2}$  for n- $\text{Ga}_2\text{O}_3$ ),  $q\phi_B$  is the effective SBH,  $R_S$  is the series resistance, and  $n$  is the ideality factor. Both the barrier height and ideality factor are calculated from the linear part in  $\ln(I)$ - $V$  curves. The flat-band barrier height is obtained from the  $C$ - $V$  characteristics under reverse bias condition. The capacitance in the Schottky diodes satisfies the following equation [23]

$$\frac{A^2}{C^2} = 2 \left( \frac{V_b - V - kT/q}{qN_D\epsilon_S\epsilon_0} \right) \quad (2)$$

where  $V_b$  is the built-in potential,  $N_D$  is the carrier concentration, and  $\epsilon_S$  the dielectric constant of semiconductor, and  $\epsilon_0$  is the vacuum permittivity. The carrier concentration is calculated from the slope of  $A^2/C^2$  versus  $V$  plot. The barrier height is obtained from  $q\phi_B^{(C-V)} = qV_0 + qV_n + kT$ , where  $V_0$  is the intercept of  $A^2/C^2$  with the voltage axis, and  $qV_n = E_C - E_F$ . The SBH from  $C$ - $V$  method is generally higher than that from  $I$ - $V$  method. This is due to the nonuniform interfacial layer and the distribution of interfacial defects at the MS interface [39]. The obtained capacitance during the  $C$ - $V$  measurement at high frequency is not sensitive to potential fluctuations for length scales smaller than the depletion width. In this case, the capacitance is the average value over the SBH values. In addition, the effect of image force lowering and tunneling on the current conduction is negligible under the flat-band condition because electric field in the semiconductor is zero. Thus, the SBHs determined from the  $C$ - $V$  method are observed to be higher than those determined from the  $I$ - $V$  method. The flat-band barrier heights can also be obtained using the ideality factor and the effective SBH obtained from the TE model [40]

$$\phi_{FB} = n\phi_{TE} - (n-1) \frac{kT}{q} \ln \left( \frac{N_C}{N_D} \right) \quad (3)$$

**Fig. 2** **a** Plot of barrier height versus  $1/2kT$  and **b** modified Richardson plot. The barrier heights at different temperatures were taken from Li et al. [43]. The inset in **a** shows a schematic band diagram of inhomogeneous Schottky barrier



where  $N_C$  is the density of states at conduction band. In identically prepared diodes on the same semiconductor, there exists normally a linear relationship between the effective SBH and the ideality factor. After obtaining the straight lines by fitting to the effective SBH versus ideality factor plots, laterally homogeneous Schottky barrier height ( $q\phi_B^{\text{hom}}$ ) can be obtained from an extrapolation of these straight lines to the image-force controlled ideality factor  $n_{if}$  [41].

Analyses on the temperature dependent  $I$ - $V$  characteristics can also be carried out, which are required for clarifying the origin of non-idealities in the Schottky barrier and attaining the detailed knowledge on the current transport mechanism and the properties of defects and the mechanism of barrier formation. One of the non-idealities is the temperature dependence of electrical parameters. For example, an increase in barrier height and a decrease in ideality factor are observed from the temperature dependent  $I$ - $V$  characteristics, which are associated with the laterally inhomogeneous Schottky barrier [42]. A Gaussian distribution of barrier heights over the Schottky contact area is assumed in this model, where the effective SBH ( $q\phi_B$ ) related with a zero-bias mean SBH ( $q\bar{\phi}_B$ ) and a standard deviation ( $\sigma_\phi$ ) is given by [42]

$$q\phi_B = q\bar{\phi}_B - q^2\sigma_\phi^2/2kT \quad (4)$$

Then, the modified Richardson plot can be obtained as follows

$$\ln\left(\frac{I_0}{T^2}\right) - \frac{q^2\sigma_0^2}{2k^2T^2} = \ln(AA^{**}) - \frac{q\phi_B}{kT} \quad (5)$$

Using Eq. (5), the modified Richardson constant ( $A^{**}$ ) is calculated.

Li et al. reported an increase in barrier height with the temperature in Ni Schottky contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [43]. Although they provided the SBH values at different temperatures, the Schottky barrier inhomogeneity was not examined using the modified Richardson plots. By taking the SBHs at different temperatures from their work [43], the characteristics of Schottky barrier in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> were analyzed in this article. Based on the linear fit to the plot of  $q\phi_B$  versus  $1/2kT$  shown in Fig. 2a, the value of  $q\bar{\phi}_B = 1.42$  eV and  $\sigma_\phi = 0.143$  V were obtained. From the linear fitting to the modified Richardson plot of  $\ln(I_0/T^2) - q^2\sigma_0^2/2k^2T^2$  versus  $1/kT$  shown in Fig. 2b, the Richardson constant was calculated to be  $35.7 \text{ Acm}^{-2} \text{ K}^{-2}$ . This is similar to the theoretical value of  $41.1 \text{ Acm}^{-2} \text{ K}^{-2}$  for n-Ga<sub>2</sub>O<sub>3</sub>, indicating that the temperature dependence of barrier heights can be explained by the inhomogeneous Schottky barrier with a Gaussian distribution of barrier heights. Li et al. also showed that the forward  $I$ - $V$  characteristics follow the thermionic field emission (TFE) model rather than TE [43]. The obtained barrier heights from TFE model were about  $1.32 \sim 1.40$  eV, which are similar to the  $q\bar{\phi}_B$  value of  $1.42$  eV, assuring again the inhomogeneous Schottky barrier for the forward current characteristics. The inset in Fig. 2(a) shows a schematic diagram of inhomogeneous Schottky barrier.

## 4 Metal contacts to $\beta\text{-Ga}_2\text{O}_3$

### 4.1 Schottky contacts to $\beta\text{-Ga}_2\text{O}_3$

Normally Schottky contacts to  $\beta\text{-Ga}_2\text{O}_3$  single crystals have been fabricated in vertical structure, in which Schottky and ohmic contacts are formed on the front and back surfaces of the samples, respectively. A  $\beta\text{-Ga}_2\text{O}_3$  epitaxial layer was used in some studies (denoted as n-epi/n-bulk), while other studies used bulk  $\beta\text{-Ga}_2\text{O}_3$  (denoted as n-bulk). Note that most of the research results were obtained by analyzing only one or two contact metals and a comprehensive investigation using various metal contacts to the same  $\beta\text{-Ga}_2\text{O}_3$  layer is still lacking. Owing to the different material quality of  $\beta\text{-Ga}_2\text{O}_3$  layer, carrier concentration, surface/interface states, and surface treatment, direct comparison between each work can result in incorrect conclusions. Hence, research results including multiple metals within the same study were discussed mainly in this article.

Table 2 shows the research results in the literature obtained from Schottky contacts to  $(\bar{2}01)$   $\beta\text{-Ga}_2\text{O}_3$ . The reported barrier heights for Ni and Pt contacts are in the range of 0.9 ~ 1.6 eV. Investigation of Schottky diodes using multiple metal contacts were performed by Yao et al. [25] and Hou et al. [56]. The Schottky metal contacts for these two works were formed on EFG-grown Sn-doped  $(\bar{2}01)$   $\beta\text{-Ga}_2\text{O}_3$  single crystals. Based on the reported SBHs, the relationships between barrier height and metal work function in Schottky contacts to  $(\bar{2}01)$   $\beta\text{-Ga}_2\text{O}_3$  were obtained, which are shown in Fig. 3a. The barrier heights show little dependence on metal work function, indicating significant Fermi-level (FL) pinning. Such FL pinning was associated with native defects or interface states located at ~ 1.3 eV below the conduction band ( $E_C$ ) [56]. Higher density of oxygen dangling bonds on the  $(\bar{2}01)$  plane was suggested as an origin of strong FL pinning. Hou et al. also reported that barriers heights of oxidized Schottky contacts were to be higher than their unoxidized metal counterparts [56]. However, the oxidized contacts also showed little correlation between barrier height and metal work function. The barrier heights of the oxidized Schottky contacts were pinned by another deep-level defect close to  $E_C - 2.0$  eV.

Table 3 shows the research results in the literature obtained from Schottky contacts to  $(001)$   $\beta\text{-Ga}_2\text{O}_3$ . Si-doped epitaxial layers grown on Sn-doped  $\beta\text{-Ga}_2\text{O}_3$  substrates were mainly examined in this orientation. Lingaparathi et al. explored the surface states on halide vapor phase epitaxy (HVPE) grown  $(001)$   $\beta\text{-Ga}_2\text{O}_3$  epilayers by determining the SBHs for different metal contacts using Cr, Cu, Ni, and Au [76]. Figure 3b shows

the plots of barrier height versus metal work function using the data taken from Lingaparathi et al. [76]. For epi-1 sample (HVPE-grown Si-doped epitaxial layer with the carrier concentration of  $2.5\text{--}3.2 \times 10^{16} \text{ cm}^{-3}$ ), the barrier height was found to be nearly pinned at 1.2 ~ 1.35 eV, closely matched with the energy level of the oxygen vacancy [ $V_O(\text{III})$ ] state ( $E_V + 3.57$  eV) in  $\beta\text{-Ga}_2\text{O}_3$ . Based on this result, they suggested that FL pinning is due to  $V_O$ -related surface states on  $(001)$  oriented  $\beta\text{-Ga}_2\text{O}_3$  epitaxial layers. In contrast, the FL was observed to be weakly pinned on the bulk and epi-2 (improved Si-doped epitaxial layer with the concentration of  $5.3\text{--}7.2 \times 10^{16} \text{ cm}^{-3}$ )  $(001)$   $\beta\text{-Ga}_2\text{O}_3$ . The density of surface states for epi-1 sample was found to be higher than those for bulk and epi-2 samples, indicating the presence of higher density of  $V_O$ -related states on the  $\beta\text{-Ga}_2\text{O}_3$  surface for epi-1 sample. In another work [77], they showed by simulation that deep donor type surface states (probably  $V_O$ ) are responsible for lowering the barrier height and increasing the reverse leakage current. Based on the results they suggested that the oxygen vacancy generated in  $(001)$   $\beta\text{-Ga}_2\text{O}_3$  epitaxial layer during the HVPE growth process affected on the SBH and the electrical properties of  $(001)$   $\beta\text{-Ga}_2\text{O}_3$  based devices.

Tables 4 and 5 show the research results in the literature obtained from Schottky contacts to  $(100)$  and  $(010)$   $\beta\text{-Ga}_2\text{O}_3$ , respectively. Studies on these orientations are rather sparse. Lyle et al. investigated six different Schottky metals to  $(100)$   $\beta\text{-Ga}_2\text{O}_3$  substrates [78]. Near-ideal average ideality factors (1.05–1.15) were found for Ti, Mo, Co, and Ni contacts, whereas higher ideality factors (~1.3) were observed for Pd and Au contacts. The electrical behavior of the Pd and Au contacts were associated with the presence of spatially inhomogeneous Schottky barriers. Figure 4a shows the plots of barrier height versus metal work function using the data taken from Lyle et al. [78], revealing a strong correlation between the calculated barrier heights and the metal work functions. Similarly, Fig. 4b shows the plots of barrier height versus metal work function for  $(010)$   $\beta\text{-Ga}_2\text{O}_3$  Schottky contacts, where the data were taken from Yao et al. [25] and Farzana et al. [88]. The barrier height is observed to be dependent on the metal work function, suggesting that metal contacts to  $(010)$   $\beta\text{-Ga}_2\text{O}_3$  are not fully pinned. According to the comparative studies on the Schottky contact to  $(\bar{2}01)$  and  $(010)$   $\beta\text{-Ga}_2\text{O}_3$  interfaces by Fu et al. [21] and Bhattacharyya et al. [22], barrier heights were found to be higher for  $(010)$  orientation compared to  $(\bar{2}01)$  orientation. Figures 5a and b show the temperature-dependent  $I$ - $V$  characteristics for  $(\bar{2}01)$  and  $(010)$   $\beta\text{-Ga}_2\text{O}_3$  Schottky diodes, respectively, reported by Fu et al. [21]. The obtained barrier heights in Figs. 5c and d show the higher values for  $(010)$  orientation. These works indicate that the crystalline anisotropy

**Table 2** Summary of Schottky contacts to  $(\bar{2} 01) \beta\text{-Ga}_2\text{O}_3$  reported in the literature

Schottky contact (thickness: nm)	Ohmic contact (thickness: nm)	Schottky contact deposition	Device structure (Growth method)	$q\phi_B$ (eV)	Ideality factor	Cleaning method	Carrier concentration ( $\text{cm}^{-3}$ )	Refs
Ni/Au (20/80)	Ti/Au (20/80)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (MOCVD/EFG)	1.22 ( <i>I-V</i> )	1.07	Patterned by lift-off	$4.02 \times 10^{15}$	[44]
Ni/Pt (50/30)	Ti/Au (75/150)	E-beam evaporation	n <sup>+</sup> -bulk	$\sim 1.2$ ( <i>I-V</i> )	1.14	Ozone, BOE (30:1), diluted HCl (1:1)	$1.45 \times 10^{18}$	[45]
Ni	Ti (100)	Sputtering	n-bulk (EFG)	1.04 ( <i>I-V</i> ) 1.12 ( <i>C-V</i> )	1.19	Solvent, Piranha	$2.8 \times 10^{17}$	[46]
Pt/Au	Ti/Al/Ti/Au	E-beam evaporation	n <sup>+</sup> -bulk (EFG)	0.94	1.39	Solvent	$\sim 3 \times 10^{18}$	[47]
Ni/Au (20/80)	Ti/Au (20/80)	E-beam evaporation	n-bulk (EFG)	1.20 ( <i>I-V</i> )	1.00	Plasma etching	$\sim 3 \times 10^{17}$	[48]
Pt/Ti/Au (50/10/100)	Ti/Au (20/100)	E-beam evaporation	n-bulk (EFG)	1.20 ( <i>I-V</i> )	1.02	Solvent, HCl:H <sub>2</sub> O for ohmic contact	-	[49]
Ni/Au (20/80)	Ti/Au (20/80)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (MOCVD/EFG)	1.07 ( <i>I-V</i> )	1.30	Patterned by lift-off	$\sim 9 \times 10^{16}$	[50]
Pt/Au (20/80)	Ti/Au (20/80)	E-beam evaporation	n-bulk (EFG)	1.04 ( <i>I-V</i> )	1.28	Patterned by lift-off	$\sim 3 \times 10^{17}$	[50]
Pt/Au (20/200)	Ti/Au (10/100)	E-beam evaporation	n-bulk (EFG)	1.01 ( <i>I-V</i> )	1.07	UV/ozone	$\sim 3 \times 10^{17}$	[51]
TiN (65)	Ti/Au (10/100)	Atomic layer deposition	n-bulk (EFG)	0.98 ( <i>I-V</i> )	1.09	UV/ozone	$\sim 3 \times 10^{17}$	[51]
Graphite carbon/Pt (40/20)	Ti/Au (20.30)	Ion-beam sputtering	n-bulk (EFG)	0.8 ~ 1.2 ( <i>I-V</i> ) 1.6 ( <i>C-V</i> )	1.08	Patterned by lift-off	$2 \times 10^{17}$	[52]
Oxidized Pd (110)	Ti/Au (50/50)	Magnetron sputtering	n-bulk (EFG)	1.45 ( <i>I-V</i> )	$\sim 1.1$	Solvent	$1.3 \times 10^{17}$	[53]
Ni/Au (150/200)	Ti/Al/Ti/Au (20/130/20/50)	E-beam evaporation	n <sup>+</sup> -bulk (EFG)	$\sim 0.9$ ( <i>I-V</i> )	$\sim 1.5$	Patterned by lift-off	$5.5 \times 10^{18}$	[54]
W/Au (100/50)	Ti/Au (20/80)	DC sputtering/E-beam evaporation	n-bulk (EFG)	0.97 ( <i>I-V</i> ) 0.92 ( <i>I-V-T</i> )	1.04	HCl/ozone	$2 \times 10^{17}$	[55]
Ru ( $\sim 40$ )	Ti/Au (50/50)	RF sputtering	n-bulk (EFG)	1.05 ~ 1.2 ( <i>I-V</i> ), 1.26 ( <i>C-V</i> )	1.05 ~ 1.15	-	$1.3 \times 10^{17}$	[56]
Ni/Au	-	evaporation	n-bulk (EFG)	1.25 ( <i>I-V</i> )	1.01	-	$\sim 1.2 \times 10^{17}$	[57]
Ni/Au (20/80)	Ti/Au (20/80)	E-beam evaporation	n-bulk (EFG)	1.20 ( <i>I-V</i> )	1.00	ICP etching	$\sim 3 \times 10^{17}$	[58]

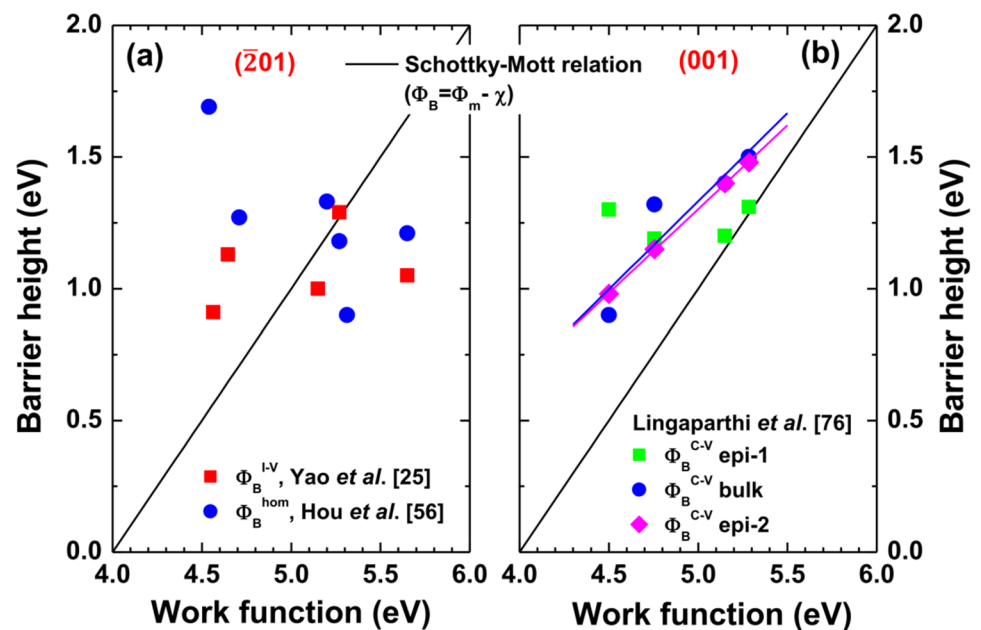
<sup>a</sup>Carrier concentration for the layer on which the Schottky contacts are formed, <sup>b</sup>Growth method: Metal organic chemical vapor deposition (MOCVD), Edge-defined film-fed growth (EFG), MOCVD/EFG: MOCVD-grown epilayer on EFG-grown substrate

of  $\beta\text{-Ga}_2\text{O}_3$  can affect the electrical properties of Schottky contacts and needs to be taken into account for device design.

Surface treatment prior to metallization is an important factor in determining the SBH and the device stability. Yao et al. investigated the effect of five different wet chemical treatments on the electrical properties of Ni/ $(\bar{2} 01) \beta\text{-Ga}_2\text{O}_3$  Schottky diodes and found that rinsing in an

organic solvent, cleaning with HCl and H<sub>2</sub>O<sub>2</sub>, and rinsing with deionized water showed the best results [25]. Based on the results they concluded that unpassivated surface states and/or bulk/near-surface defects are more dominant in determining the electrical behavior of these diodes compared to the choice of different Schottky metals. Yang et al. characterized the effect of various surface treatments such as gaseous (ultraviolet/O<sub>3</sub>), liquid (HCl, buffered oxide

**Fig. 3** Plots of barrier height versus metal work function for **a**  $(\bar{2}01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky contacts using the barrier heights taken from Yao et al. [25] and Hou et al. [56] and **b** (001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky contacts using the barrier heights taken from Lingaparathi et al. [76]. The metal work functions were taken from ref. [24]



etch), or plasma (CF<sub>4</sub> and O<sub>2</sub>) on the properties of Ni/(001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes [94]. Standard chemical cleaning involving UV/O<sub>3</sub> or acid was found not to degrade the near-surface electrical properties whereas plasma treatment induced surface damage acting as generation-recombination centers. To date, however there is limited work on such systematic investigation using various surface treatments for the same  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> surface.

According to the review on Schottky contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, we can summarize the following points. (1) Significant FL pinning is observed for the Schottky contacts to  $(\bar{2}01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> due to presence of surface and/or near surface defects. The possible origin of such defects is suggested to be oxygen vacancy-related defects. (2) Correlations between the barrier height and metal work function are observed for (001), (100) and (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, suggesting that metal work function affects the barrier height on these orientations. (3) Compared to  $(\bar{2}01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> revealed higher barrier height, associated with the larger surface band bending [21]. (4) When the surface defects are generated during the epitaxial growth, the FL pinning can occur [76]. Therefore, optimizing growth conditions for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> epitaxial layer is pivotal to improve the device performance. (5) Mostly Schottky metals were deposited by using e-beam evaporation. For other semiconductors (e.g., GaN [95]), different barrier heights were obtained according to the deposition methods. This point needs to be explored for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes more thoroughly.

As a modulating method for diode characteristics, an interfacial layer (IL) between metal and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> was proved to yield useful results. He et al. formed about 4 nm

thick Al<sub>2</sub>O<sub>3</sub> IL between Ni/Au and  $(\bar{2}01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrate by annealing the sputtered Al layer at 300 °C in O<sub>2</sub> atmosphere [96] and observed the improved diode characteristics, with respect to the sample without IL. Further, they showed that this Al-reacted IL exhibited better performance than the sample with the Al<sub>2</sub>O<sub>3</sub> IL prepared by atomic layer deposition (ALD). Harada and Tsukazaki deposited PdCoO<sub>2</sub> layer on  $(\bar{2}01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrate by pulsed laser deposition (PLD) and fabricated the stacked Schottky contacts composed of various metals (Pt, Ni, Cr, and Ti) [97]. As shown in Fig. 6, they found that the barrier height systematically increased from 0.7 to 1.9 eV with the increase in the thickness of PdCoO<sub>2</sub> from 0 to 20 nm by selecting suitable combination of top metal and thickness of PdCoO<sub>2</sub>. The PdCoO<sub>2</sub> layer consisted of alternately stacked ionic Pd<sup>+</sup> and [CoCo<sub>2</sub>]<sup>-</sup> sublattices, which spontaneously induced interface dipoles that increased the SBH in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes. Bhattacharyya et al. deposited about 3 nm thick SiO<sub>2</sub> IL by ALD on (010),  $(\bar{2}01)$  and (100)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrates and observed the increase in barrier height for all orientations [22]. Especially, the Schottky contacts to (100)-oriented substrates exhibited a dramatic increment in barrier height and a reduction in reverse leakage current. These works suggest a strong potential of IL as a method to modulate the diode characteristics, however, these kinds of works are hardly observed.

The strong light absorption of metal contacts can limit the development of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky-junction-based photonic devices. Due to the excellent properties such as high optical transmittance, large electrical conductivity, and a tunable work function, graphene is a good

**Table 3** Summary of Schottky contacts to (001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> reported in the literature

Schottky contact (thickness: nm)	Ohmic contact (thickness: nm)	Schottky contact deposition	Device structure (Growth method)	$q\phi_B$ (eV)	Ideality factor	Cleaning method	Carrier concentration (cm <sup>-3</sup> )	Refs
Ni/Au (40/160)	Ti/Au (20/80)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE/EFG)	1.03 ( <i>I</i> - <i>V</i> )	1.1	Ozone, BOE	$2.1 \times 10^{15}$	[59]
Ni/Au (40/160)	Ti/Au (20/80)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE/EFG)	1.04 ( <i>I</i> - <i>V</i> )	1.02	Ozone, BOE	$1.33 \times 10^{16}$	[60]
Pt/Ti/Au (20/100/100)	Ti/Al/Au (50/150/200)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE for epi)	-	1.02	Patterned by lift-off	$4 \times 10^{16}$	[61]
Ni/Au (20/80)	Ti/Au (20/80)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE/EFG)	-	-	Patterned by lift-off	$\sim 3 \times 10^{16}$	[62]
Ni/Au	Ti/Au (30/150)	-	n-epi/n <sup>+</sup> -bulk (HVPE for epi)	1.2 ( <i>I</i> - <i>V</i> )	1.08	Diluted HF, wet etching	$\sim 1.5 \times 10^{16}$	[63]
ITO (100)	Ti/Au (20/80)	DC sputtering	n-epi/n <sup>+</sup> -bulk (HVPE for epi)	1.15 ( <i>I</i> - <i>V</i> ) 1.24 ( <i>C</i> - <i>V</i> )	$\sim 1.1$	HCl, ozone	$\sim 3 \times 10^{16}$	[64]
Ni/Au (30/250)	Ti/Au (20/80)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE/EFG)	1.02 ( <i>I</i> - <i>V</i> ) 1.26 ( <i>C</i> - <i>V</i> )	1.17	Patterned by lift-off	$6.9 \times 10^{15}$	[65]
W/Au (20/80)	Ti/Au (20/80)	DC sputtering/ E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE/EFG)	0.71 ( <i>I</i> - <i>V</i> )	1.30	HCl, ozone	$3.5 \times 10^{16}$	[66]
Ni/Au (200)	Ti/Au	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE for epi)	1.23 ( <i>I</i> - <i>V</i> )	1.05	BOE	$1.6 \times 10^{16}$	[67]
Ni/Au (20/80)	Ti/Au (20/80)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE/EFG)	1.1 ( <i>I</i> - <i>V</i> )	1.08	Patterned by lift-off	$\sim 2 \times 10^{16}$	[68]
Pt/Ti/Au (15/5/500)	Ti/Au (20/230)	Evaporation	n-epi/n <sup>+</sup> -bulk (HVPE/EFG)	1.46 ( <i>I</i> - <i>V</i> - <i>T</i> )	-	Solvent, acid cleaning	$1 \times 10^{16}$	[69]
Ni/Au (80/420)	Ti/Au	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE/EFG)	1.05 ( <i>I</i> - <i>V</i> )	1.03	BOE	$2.01 \times 10^{15}$	[70]
Ni/Au	Ti/Al/Ni/Au	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE/EFG)	0.98 ( <i>I</i> - <i>V</i> )	1.13	BOE	$\sim 1.5 \times 10^{16}$	[71]
Pt/Ti/Au (15/5/250)	Ti/Au (20/230)	Evaporation	n-epi/n <sup>+</sup> -bulk, (HVPE/EFG)	1.09~1.15 ( <i>I</i> - <i>V</i> )	$\sim 1.0$	Acid cleaning	$1.4 \times 10^{16}$	[72]
Ni/Au	Ti/Au	-	n-epi/n <sup>+</sup> -bulk, (HVPE for epi)	1.09 ( <i>I</i> - <i>V</i> )	1.06	-	$2\text{--}3 \times 10^{16}$	[73]
Ni/Au (20/60)	Ti/Au (20/80)	Thermal evaporation	n-epi/n <sup>+</sup> -bulk, (HVPE/EFG)	1.27 ( <i>I</i> - <i>V</i> ) 1.38 ( <i>C</i> - <i>V</i> )	1.14	Solvent, sulfuric-peroxide mixture (SPM)	$1 \times 10^{16}$	[74]
Ni/Au (80/300)	Ti/Au (20/80)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (HVPE/EFG)	1.14 ( <i>I</i> - <i>V</i> )	1.02	UV ozone/HCl: DI (1:10)	$2.8 \times 10^{16}$	[75]
Cr (20)	Ti/Au (50/250)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk, (HVPE/EFG)	$\sim 1.3$ ( <i>C</i> - <i>V</i> )	-	HF, piranha/solvent	2.5– $3.2 \times 10^{16}$	[76]
Ni/Au (20/230)	Ti/Au (50/230)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk, (HVPE/EFG)	1.15 ( <i>I</i> - <i>V</i> )	1.09	Patterned by lift-off	2.4– $3.5 \times 10^{16}$	[77]

<sup>a</sup>Carrier concentration for the layer on which the Schottky contacts are formed, <sup>b</sup>Growth method: Hydride vapor phase epitaxy (HVPE), Edge-defined film-fed growth (EFG), HVPE/EFG: HVPE-grown epilayer on EFG-grown substrate

alternative for transparent electrodes. Graphene/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> contacts has been studied for the applications of photosensors [9, 98–102]. Graphene/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky contacts have also been applied for other devices. The graphene/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> contact in the double graphene-gate  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> metal – semiconductor FET (MESFET) operated in the enhancement-mode were found to have a barrier height of  $\sim 0.62$  eV and an ideality factor of 1.5 [100]. Yan et al.

reported the high critical breakdown field of 5.2 MV/cm in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> perpendicular to the (100) crystal plane using a vertical graphene/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> heterostructure [101]. Kim et al. examined high-performance solar-blind photodetectors based on mechanically exfoliated  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> flakes and found that their photoresponsivity was enhanced significantly with UV-transparent graphene electrodes [102]. They also suggested that the high optical transparency



**Table 4** Summary of Schottky contacts to (100)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> reported in the literature

Schottky contact (thickness: nm)	Ohmic contact (thickness: nm)	Schottky contact deposition	Device structure (Growth method)	$q\phi_B$ (eV)	Ideality factor	Cleaning method	Carrier concentration (cm <sup>-3</sup> )	Refs
Co (30)	Ti/Au (20/100)	E-beam evaporation	n-bulk (CZ)	1.06 ( $I-V$ ) 1.35 ( $I-V-T$ )	1.06	10% HCl, H <sub>2</sub> O <sub>2</sub> boiling	$5 \times 10^{17}$	[78]
Pd (20)	Ti/Au (20/100)	E-beam evaporation	n-bulk (CZ)	$\sim 1.34$ ( $I-V$ ) $\sim 1.81$ ( $I-V$ )	$\sim 1.31$	10% HCl, H <sub>2</sub> O <sub>2</sub> boiling	$4.99 \times 10^{17}$	[79]
Ni/Au (40/100)	Ti/Au (20/100)	E-beam evaporation	flakes	$\sim 1.14$ ( $I-V$ )	$\sim 1.32$	Patterned by lift-off	$7 \times 10^{16}$	[80]
Pt/Ti/Au (20/10/50)	Ti/Au (10/230)	Sputtering	n-bulk (EFG)	1.38 ( $I-V-T$ )	1.1	Patterned by lift-off ICP etching for ohmic contact	$2.3 \times 10^{14}$	[81]
Pt/Au (50/150)	Ti/Au (50/250)	E-beam evaporation	n-bulk (EFG)	-	1.09	Patterned by lift-off Solvent	-	[82]
Au (50)	Ga-In	E-beam evaporation	n-bulk (CZ)	1.07 ( $I-V$ )	1.02	-	$0.6-8 \times 10^{17}$	[83]
Ni/Au (20/150)	Ti/Au (50/300)	E-beam evaporation	n-epi/n-bulk (CZ)	1.25 ( $C-V$ )	-	Solvent, ICP etching for ohmic contact	$1.76 \times 10^{17}$	[84]
Ni/Au (30/200)	Ti/Au (20/100)	E-beam evaporation	n-bulk (EFG)	1.22 ( $I-V$ ) 1.32 ( $C-V$ )	1.06	Patterned by lift-off	$1.3 \times 10^{17}$	[85]
Ni/Au (30/100)	Ti/Au (30/100)	E-beam evaporation	n-bulk (EFG)	0.93 ( $I-V$ )	1.34	Patterned by lift-off	$4.36 \times 10^{17}$	[86]

<sup>a</sup>Carrier concentration for the layer on which the Schottky contacts are formed), <sup>b</sup>Growth method: Czochralski (CZ), Edge-defined film-fed growth (EFG)

of graphene gate prevents the shadowing effect under UV-C illumination, enabling carriers to be generated at the graphene/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> junction. Using the first-principles calculations, Yuan et al. suggested the following points in graphene/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> contacts [103]: (1) the small n-type Schottky barrier of  $\sim 0.07$  eV is irrespective of the interface stacking arrangement and the intrinsic electronic property of Ga<sub>2</sub>O<sub>3</sub> hardly alters in the interface, (2) the n-type Schottky barrier to ohmic contact transition can be obtained by shorting the interlayer distance, or increasing the graphene layers or applying a negative external electric field, and (3) applying a large positive external electric field can realize the p-type Schottky barrier to ohmic contact transition. These results will expand the application of graphene/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based devices further.

## 4.2 Ohmic contacts to $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

In order to realize high performance devices, it is essential to obtain good ohmic contact with low resistance and high thermal stability/reliability. High quality ohmic contact to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> can be formed when the Schottky barrier is low and/or the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> layer is heavily doped for the carriers

to tunnel through the barrier. In general, the specific contact resistivity ( $\rho_c$ ), typically expressed in  $\Omega\text{-cm}^2$ , is used as a parameter to assess the quality of ohmic contacts [104, 105]. The most common ohmic contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> are composed of Ti/Au metallization with post deposition annealing. Table 6 shows the research results on ohmic contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> in the literature.

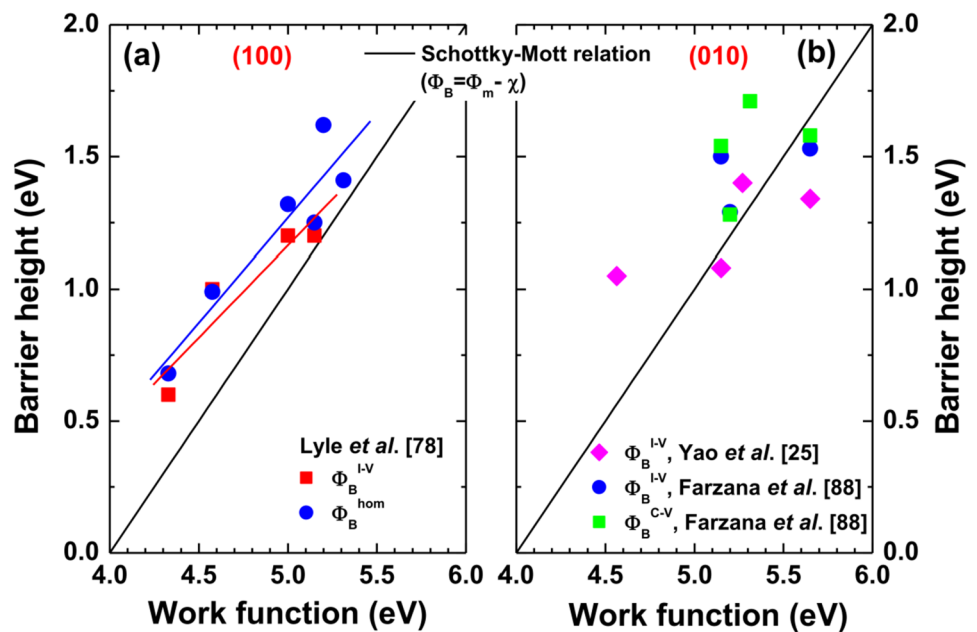
As a way of improving ohmic contact properties, Si-ion implantation was employed to create a heavy doped n<sup>+</sup>-region that facilitates electron tunneling across the junction [106–108, 110, 111]. However, this process requires high temperature annealing (> 900 °C) to electrically activate Si donors. Ozone molecular beam epitaxy (MBE) was also used to grow highly doped epitaxial layer [112]. Meanwhile, Yao et al. reported that the contact resistance of Ti/Au metallization is associated with the limited interfacial reactions between the metal and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [113]. They observed that Ti began to react with the Ga<sub>2</sub>O<sub>3</sub> at annealing temperatures above 400 °C and formed an insulating oxide layer, increasing the contact resistance. In addition, they investigated the ohmic properties of nine metals (Ti, In, Ag, Sn, W, Mo, Sc, Zn and Zr) with an Au capping layer and concluded that metal work function is not

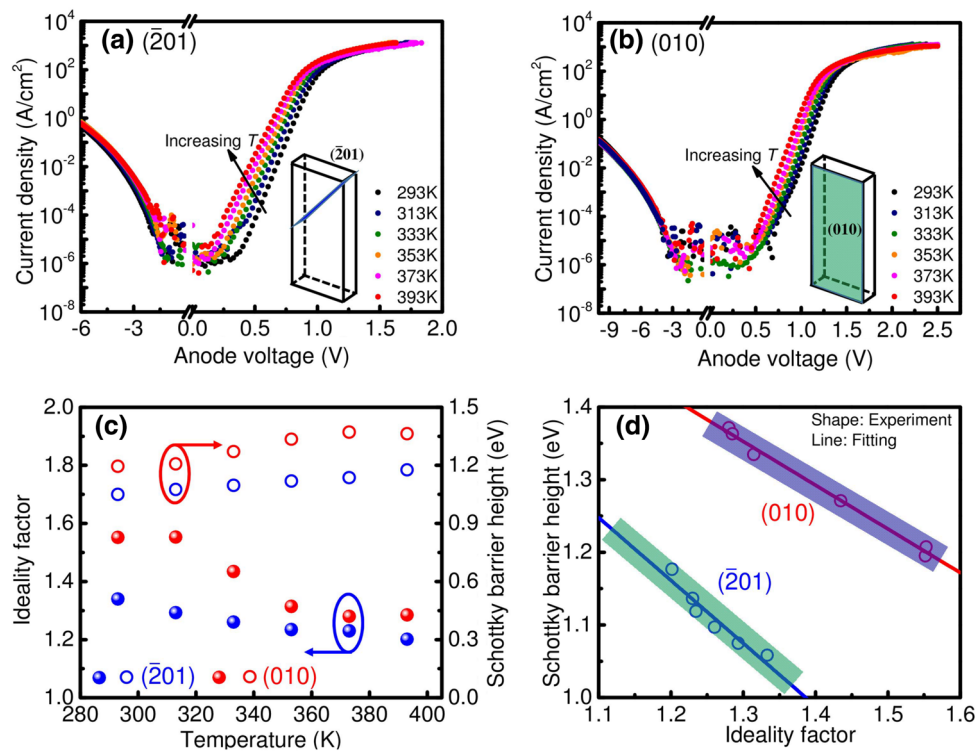
**Table 5** Summary of Schottky contacts to (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> reported in the literature

Schottky contact (thickness: nm)	Ohmic contact (thickness: nm)	Schottky contact deposition	Device structure (Growth method)	$q\phi_B$ (eV)	Ideality factor	Cleaning method	Carrier concentration (cm <sup>-3</sup> )	Refs
Pt/Au	Ti/Al/Ti/Au	E-beam evaporation	n-bulk (EFG)	1.20 (I-V) 1.30 (C-V)	1.55	ICP etching for ohmic contact	$4.3 \times 10^{18}$	[21]
Ni/Au (50/150)	Ti/Au (50/50)	E-beam evaporation	n-bulk (VGF)	1.27 (I-V) 1.50 (C-V)	1.16	Solvent, Piranha	$1.1 \times 10^{18}$	[22]
Ni/Au (20/100)	Sn	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (EFG)	0.95 (I-V)	3.38	-	-	[87]
Ni (8)	Ti/Al/Ti/Au (total ~430)	E-beam evaporation	n-bulk (EFG)	1.50 (I-V) 1.54 (C-V)	1.04	RIE etching for ohmic contact	$\sim 1.1 \times 10^{17}$	[88]
Ni/Au (10/30)	Ti/Au (100/100)	Evaporation	n-bulk (0 $\bar{1}$ 0) (EFG)	1.08 (I-V)	1.1	-	$1-2.5 \times 10^{17}$	[89]
Pt/Ti/Au (20/10/30)	Ti/Au (20/40)	Magnetron sputtering	n-bulk (EFG)	1.10 (I-V)	1.16	Oxygen plasma for ohmic contact	2.29– $2.31 \times 10^{17}$	[90]
Pt/Ti/Au (15/5/250)	Ti/Au (20/230)	Evaporation	n-bulk (FZ)	1.36 (I-V) 1.52 (C-V)	-	Solvent, 46% HF, H <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O <sub>2</sub>	$3 \times 10^{16}$	[91]
Pt/Au/Ni	Ti/Au/Ni	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (LPCVD for epi)	1.5 (C-V)	1.03	ICP-RIE etching for patterning	$2.5 \times 10^{17}$	[92]
Pt/Au (40/30)	Ti/Au (30/120)	E-beam evaporation	n-epi/n <sup>+</sup> -bulk (MOCVD for epi)	-	1.01	ICP etching for sidewall Schottky	$1 \times 10^{15}$	[93]

<sup>a</sup>Carrier concentration for the layer on which the Schottky contacts are formed, <sup>b</sup>Growth methods: Czochralski (CZ), Edge-defined film-fed growth (EFG), Vertical gradient freeze (VGF), Floating zone (FZ), Low pressure chemical vapor deposition (LPCVD), Metal organic chemical vapor deposition (MOCVD)

**Fig. 4** Plots of barrier height versus metal work function for **a** (100)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky contacts using the barrier heights taken from Lyle et al. [78] and **b** (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky contacts using the barrier heights taken from Yao et al. [25] and Farzana et al. [88]. The metal work functions were taken from ref. [24]



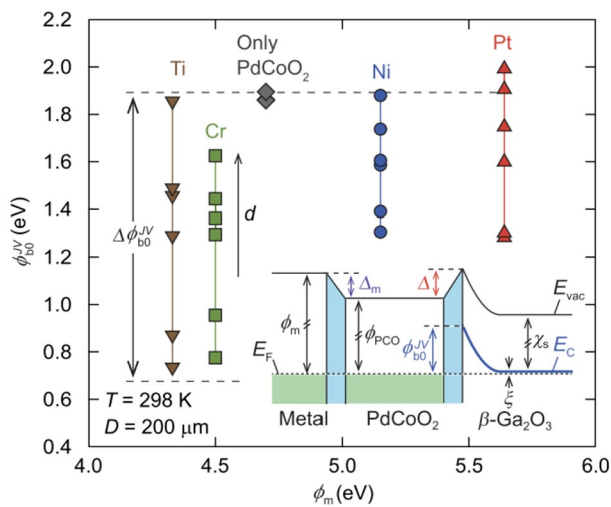


**Fig. 5** Temperature-dependent  $I$ - $V$  characteristics for **a**  $(\bar{2}01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diode and **b** (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diode, **c** ideality factor and SBH as a function of temperature, and **d** SBH versus ideality factor [21]

dominant in determining ohmic contact to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> but interfacial reaction gives a significant effect on the morphology and electrical behavior. Li et al. could suppress the contact resistance between Ti and Ga<sub>2</sub>O<sub>3</sub> by annealing in Ar ambient [114]. However, they also observed the degraded contact property when annealed above 500 °C. This was associated with the formation of a thicker TiO<sub>x</sub> non-/low conductive layer [115]. Therefore, most works utilized the annealing temperature between 400 and 500 °C for the Ti/Au ohmic contact. Lee et al. carried out a study on the interdiffusion and interfacial reactions of the ohmic contact between Ti/Au and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [116]. As shown in Fig. 7, they could observe a defective  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> layer, a Ti-TiO<sub>x</sub> layer, and an intermixed Au-Ti layer containing Ti-rich nanocrystalline products after annealing. After in-situ annealing with O pressure of 100 Pa at 800 °C for 2 h, Guo et al. observed that the contact exhibited a conversion from ohmic behavior to Schottky behavior, associated with the decrease of concentration of oxygen vacancies [117]. The instability of the Ti/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> interface using Ti/Au metal scheme needs to be improved with enhanced thermal stability. Hence, more comprehensive understanding of interfacial reactions can increase the potential of Ti based ohmic contacts.

Including Si ion implantation, plasma bombardment and reactive ion etching (RIE) has also been studied as

other pretreatments prior to the metallization. Higashiwaki et al. showed that the Schottky-like Ti/Au contacts became ohmic-like with the RIE process, which were associated with the generation of oxygen vacancies resulted from the out-diffusion of the oxygen atoms [118]. Zhou et al. also demonstrated that Ar plasma bombardment for 30 s could reduce the contact resistance by enhancing surface n-type doping [119]. Using both RIE and Si ion implantation, the specific contact resistance was reported to be  $8.1 \times 10^{-6} \Omega \cdot \text{cm}^2$  [120]. This suggests that the ohmic contact properties can be enhanced by using both RIE and Si ion implantation. Surface defects are introduced at the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> surface during the RIE etching and ion bombardment. Then, these defects can act as carrier recombination centers after metallization, reducing contact resistance. As another method to heavily dope  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, Zeng et al. employed spin-on-glass (SOG) method with a high-temperature diffusion drive-in process at 1200 °C for 5 min to obtain heavy Sn-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [121]. The specific contact resistance was found to be  $\sim 2.1 \times 10^{-5} \Omega \cdot \text{cm}^2$ . Xia et al. reported a contact resistance of  $\sim 1.5 \Omega \cdot \text{mm}$  by using a recess and MBE regrown Si delta doping with a carrier concentration of  $\sim 2 \times 10^{20} \text{ cm}^{-3}$  [122]. Based on the reported results, it is speculated that a heavily doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> layer can be obtained by various doping techniques, resulting in the specific contact resistance of  $10^{-5} \sim 10^{-6} \Omega \cdot \text{cm}^2$ .



**Fig. 6** Plots of barrier height versus metal work function for metal/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> contacts with a PdCoO<sub>2</sub> interlayer (IL). With increasing the thickness  $d$  of PdCoO<sub>2</sub> IL from 0 to 20 nm, the barrier height was found to increase. The inset shows the possible band diagram with a PdCoO<sub>2</sub> (IL). (Reprinted from ref. 97, under the terms of the Creative Commons CC BY 4.0 license)

As shown in Table 6, some works employed indium tin oxide (ITO) and aluminum zinc oxide (AZO) as an IL between ohmic metals and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> layer [107, 108]. This ohmic contact scheme can be realized with a relatively low doping concentration ( $\sim 10^{17}$  cm<sup>-3</sup>) of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> by post-annealing alone and maintain their ohmic property even after annealing above 1150 °C [108]. These are advantageous compared to Ti-based electrodes, simplifying the device fabrication process and realizing high-temperature operating devices. As shown in Fig. 8, no bubbling was observed on the surface of ITO/Ti/Au contacts while a bubble was observed after annealing at 500 and 600 °C, resulted from the out-diffusion of oxygen atoms into the upper metal layers [110]. Thus, it is required to cap ITO layers with different metal layers to prevent the degradation of surface morphology.

Recently, Lyle et al. fabricated Ti/Au metal contacts on (010) and (001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> layers and investigated the interfacial characteristics as a function of annealing temperature [26]. They observed significant differences in the chemical and electrical properties of the Ti/(010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and Ti/(001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> interfaces: 1) larger amounts of Ti-oxidation observed on the (001) surface, 2) higher barrier heights on the (010) surface, and 3) changes in the barrier heights for higher temperature annealing and the increase in Ti-oxidation with increasing the temperature. Based on these results, they suggested that the electrical properties of Ti-based contacts depend on the orientation of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> layer. However, such comparison between different crystal orientations is still lacking and thus more systematic study

on the orientation-dependent ohmic contact properties is necessary.

To develop the ohmic contact properties further for n-type  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, the work function of contact metal should be close or smaller than the electron affinity of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (4.0 eV [1, 83]). Accordingly, low work function metals such as Hf (work function 3.9 eV), Sc and La (both 3.5 eV) and Gd (2.9 eV) and bilayers of these with Au can be considered as alternatives to Ti/Au [123]. Shi et al. investigated the ohmic contact properties using Mg/Au metallization [124], where the work function of Mg is 3.66 eV [24].

Like Schottky contact, the transport mechanisms for ohmic contact make us to understand the electrical properties of ohmic contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> thoroughly. According to TE, thermionic field emission (TFE), and field emission (FE) models, the specific contact resistivities are described as [104, 105]

$$\rho_C \propto \frac{1}{T} \exp\left(\frac{q\phi_B}{kT}\right), \text{ for TE} \quad (6)$$

$$\rho_C \propto \exp\left(\frac{q\phi_B}{E_{00}}\right), \text{ for TFE \& FE} \quad (7)$$

Here,  $E_{00} = q\hbar/2(N_D/m_e\epsilon_s)^{1/2}$  is the energy parameter, where  $m_e$  is the electron effective mass. The current transport mechanism is different according to the  $E_{00}$  value, such as TE for  $E_{00}/kT < < 1$ , TFE for  $E_{00}/kT \sim 1$ , and FE for  $E_{00}/kT > > 1$  [104]. When no significant temperature dependence of the contact resistance is observed, it would imply that the FE model is dominant. In spite of the importance, clarifying the current transport mechanism in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> ohmic contact has rarely been done. As an example, Shi et al. [125] investigated the carrier transport mechanism of Mg/Au ohmic contact to lightly doped ( $\bar{2}01$ )  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. They found that the basic mechanism of current transport is dominated by TE model with the effective barrier height of 0.1 eV.

To summarize this section, following points are suggested to be investigated further. Ion implantation requires a high-temperature annealing process to activate the implanted donor, which may cause incomplete activation and surface roughening. Epitaxial growth can produce a high quality of epitaxial layer, but it has some drawbacks such as high expense and low throughput. Hence further studies are necessary to optimize the heavy doping process of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. Though Ti/Au metallization is widely used for ohmic contacts, other metallization can be investigated. For GaN, Ti/Al/X/Au (X=Ti, Ni, Pt...) multilayers were reported to be good ohmic contacts [126]. Some materials such as TiO<sub>2</sub>, ITO and AZO reveal the negative conduction band offset ( $\Delta E_C$ ) with  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [127]. When such materials are used as an IL, current can flow through the IL without obstruction under the forward bias while

**Table 6** Summary of ohmic contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> reported in the literature

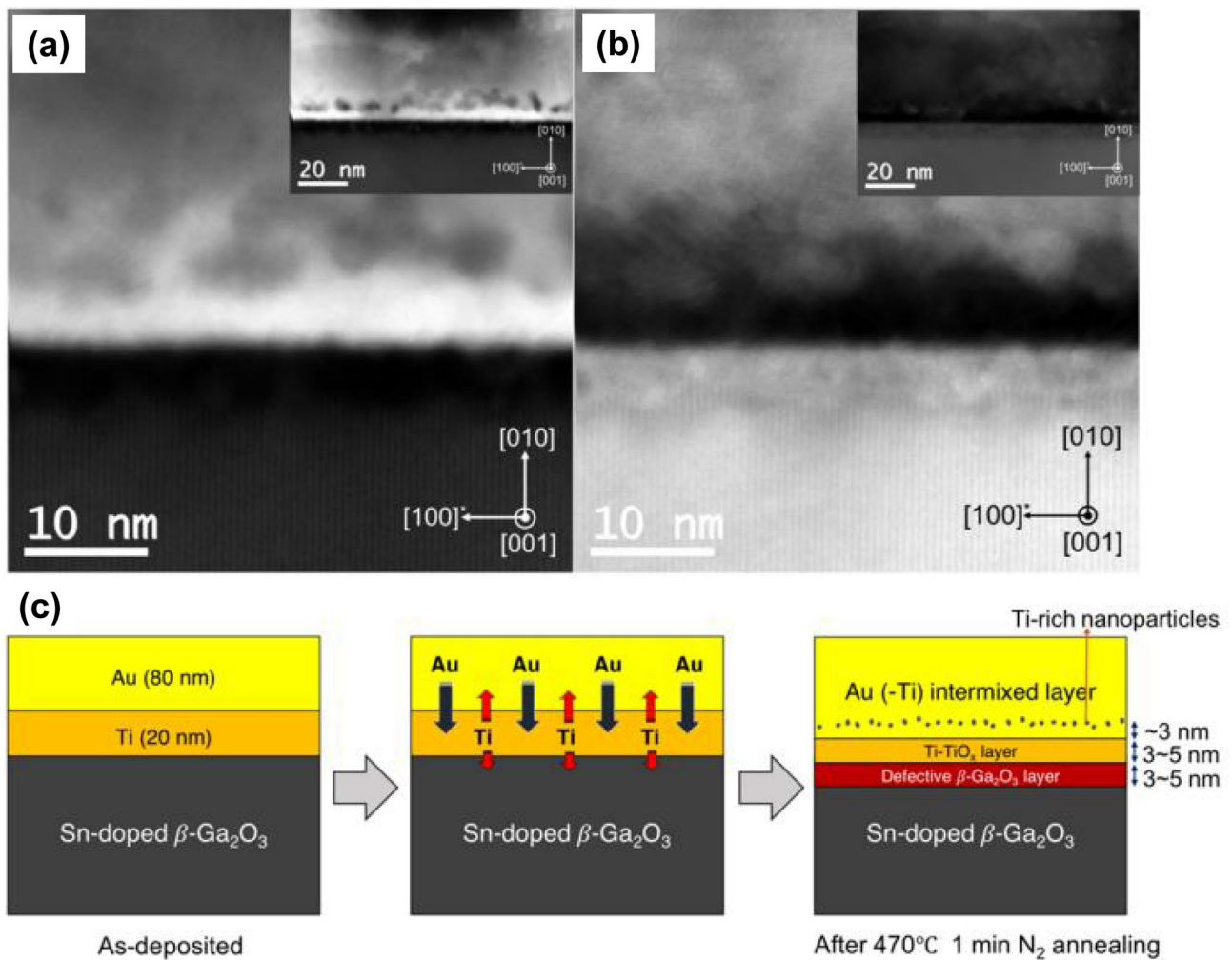
Ohmic contact (thickness: nm)	Thermal annealing	Cleaning method	Ga <sub>2</sub> O <sub>3</sub> type (Growth method)	$\rho_c$ ( $\Omega\cdot\text{cm}^2$ )	Carrier concentration ( $\text{cm}^{-3}$ )	Brief description	Refs
Ti/Au (50/300)	450 °C, 1 min (N <sub>2</sub> ambient)	Lift-off	n-epi/n-bulk (010) (MBE/FZ)	$4.6 \times 10^{-6}$	$1-5 \times 10^{19}$	Si-ion implantation on MBE grown epilayer	[106]
Ti/Au (20/230)	470 °C, 1 min (N <sub>2</sub> ambient)	-	n-epi/bulk (010) (MBE for epi)	$7.5 \times 10^{-6}$	$5 \times 10^{19}$	Si-ion implantation on MBE grown epilayer, Characterizing enhanced-mode MOS-FET	[107]
AZO/Ti/Au (20/20/80)	400 °C (N <sub>2</sub> ambient)	HCl:DI (1:10)	n-bulk ( $\bar{2}$ 01) (EFG)	$2.82 \times 10^{-5}$	$\sim 2.2 \times 10^{17}$	Si-ion implantation on bulk, AZO by RF sputtering	[108]
ITO/Pt (140/100)	800~1200 °C, 30 s (N <sub>2</sub> ambient)	-	n-bulk (010)	-	$2 \times 10^{17}$	ITO by RF sputtering, linear <i>I-V</i> when annealed at 900~1150 °C	[109]
ITO/Ti/Au (10/20/80)	500, 600 °C, 30 s (N <sub>2</sub> ambient)	HCl:DI (1:1)	n-bulk ( $\bar{2}$ 01) (EFG)	$6.3 \times 10^{-5}$	$3 \times 10^{17}$	Si-ion implantation on bulk, ITO by RF sputtering	[110]
Ti/Au	470 °C, 1 min (N <sub>2</sub> ambient)	Solvent, RIE etching	n-bulk (010) (MBE/EFG)	$3.93 \times 10^{-5}$	$\sim 3 \times 10^{19}$	Si-ion implantation on bulk, activated at 950/975 °C	[111]
Ti/Au/Ni	520 °C	-	Not reported	$2.7 \times 10^{-4}$	$1.5 \times 10^{19}$	MBE grown epilayer on Si substrate	[112]
Mg/Au (820/600)	500 °C, 2 min	Solvent, Piranha	n-bulk ( $\bar{2}$ 01)	$2.1 \times 10^{-5}$	$4 \times 10^{17}$	Annealing at 400 °C showed better stability than 500 °C	[124]

. <sup>a</sup>Carrier concentration for the layer on which ohmic contacts are formed, <sup>b</sup>Growth method: Molecular beam epitaxy (MBE), Edge-defined film-fed growth (EFG), Floating zone (FZ). MBE/FZ (EFG): MBE-grown epilayer on FZ (EFG)-grown substrate

electrons can tunnel through the triangular barrier at the IL/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> interface under the reverse bias, increasing the current values [127]. Therefore, ohmic contact properties with an optimized IL is expected to reduce the ohmic contact resistance further. Like dry plasma etching, wet etching can also affect the ohmic contact properties. Studies on the effect of wet etching on  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> ohmic contacts are lacking, requiring further investigations.

## 5 Reverse leakage current in $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

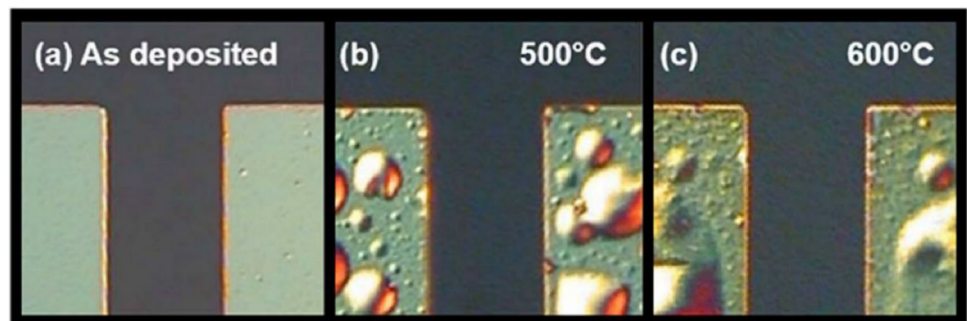
When the defects are present in the semiconductor, they can increase the reverse leakage current and decrease the breakdown voltage. Recently, much research has been done to clarify the relationship between defects and reverse leakage current in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes. Based on the analysis on the leakage current in Schottky diode array formed on (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, Kasu et al. [89] found that the dislocation defects along the [010] direction acted as leakage current sources while Si doping concentration was not associated with the leakage current. In another work, Kasu et al. [128] observed following etch pits on the ( $\bar{2}$ 01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> surface: (1) line-shaped etch pattern originated



**Fig. 7** **a** High-angle annular dark field and **b** bright field scanning transmission electron microscopy (STEM) images of Ti/Au metallization on Sn-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> after annealing at 470 °C for 1 min. Insets are the field of view in low magnification. The images show, from the bottom to top, the Ga<sub>2</sub>O<sub>3</sub> substrate, a defective Ga<sub>2</sub>O<sub>3</sub>

region, a Ti-TiO<sub>x</sub> region, an Au rich layer, Ti- or TiO<sub>x</sub>-rich nanoparticles, and Au-Ti intermixed layer. **c** Schematic illustrations of the evaluation of the Ti/Au metallization layers on Sn-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> by thermal annealing. (Reprinted from ref. 116, under the terms of the Creative Commons CC BY 4.0 license)

**Fig. 8** Optical micrographs of metal patterns on Au/Ti/ITO/Ga<sub>2</sub>O<sub>3</sub> for **a** as-deposited, **b** after 500 °C annealing, and **c** 600 °C annealing [110]



from a void defect and (2) arrow-shaped etch pit and gourd-shaped etch pit originated from a dislocation. Further, they suggested that there is no relationship between

the defects and the leakage current in vertical Schottky diodes, unlike the case for the (010) surface. Although the etch pit density on the (2̄01) surface was higher than that

on the (010) surface, the number of Schottky diodes with a high leakage current was much lower for the  $(\bar{2}01)$  surface compared to the (010) surface.

Sdoeung et al. utilized ultra-high sensitive emission microscopy to investigate the origin of reverse leakage current for EFG-grown (001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky barrier diodes [129]. They observed that the reverse leakage current is associated with the partially appearing voids on the surface but could not observe clear relationship between the leakage current path and the dislocations by synchrotron X-ray topography. Oshima et al. found in Schottky diodes on (001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> that the electrical properties such as barrier height, ideality factor and leakage current revealed almost no correlation with the density of the line-shaped voids [130]. Stacking faults, one of the killer defects, were considered to be responsible for the leakage current in Schottky contacts to HVPE-grown (001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [131]. These works indicate that the leakage current sources would be different according to the growth methods and crystal orientations.

The transport mechanisms to explain the reverse leakage current include TE, TFE, and FE models. In general, the dominant transport mechanism depends on the doping concentrations: TE for  $N_D < 1 \times 10^{17} \text{ cm}^{-3}$ , TFE for  $1 \times 10^{17} < N_D < 1 \times 10^{19} \text{ cm}^{-3}$ , and FE for  $N_D > 1 \times 10^{19} \text{ cm}^{-3}$ . When the image-force barrier lowering is present, it can also affect the reverse leakage current. According to TE and TFE models, following equations can be used to analyze the reverse  $I$ - $V$  characteristics [23, 132, 133]

$$J^{TE} = A^{**} T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \quad (8)$$

$$J^{TFE} = \frac{A^{**} T}{k} \sqrt{\pi E_{00} q \left[ V_R + \frac{\phi_B}{\cosh^2(E_{00}/kT)} \right]} \times \exp\left(-\frac{q\phi_B}{E_0}\right) \exp\left(-\frac{qV_R}{\epsilon'}\right) \quad (9)$$

$$\epsilon' = \frac{E_{00}}{E_{00}/kT - \tanh(E_{00}/kT)}, E_0 = E_{00} \coth(E_{00}/kT) \quad (10)$$

where  $\xi = \sqrt{2qN_D/\epsilon_S(V_R + V_b - kT/q)}$  is the electric field at the MS interface, and  $V_R$  is the reverse bias voltage. The reverse leakage current in Schottky diodes for wide band-gap semiconductors such as GaN, SiC, and diamond is generally explained by TFE rather than TE, in which the relatively large barrier height hinders thermal emission over the Schottky barrier but renders tunneling through the barrier [69]. This explanation can also be considered for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes.

When the defects are involved with the leakage current, Poole–Frenkel (PF) emission, one-dimensional variable range hopping (1D-VRH), and trap assisted

tunneling (TAT) may contribute to the current conduction [134–136]. Fowler–Nordheim (FN) tunneling is another possible transport mechanism, which becomes dominant when the barrier is thin enough ( $< 10 \text{ nm}$ ) [135]. The PF emission is associated with the electron emission via a trap state into a continuum of electron states [134, 135]. When the PF emission is the dominant transport mechanism, the reverse current is described by the following equation

$$J \propto \xi \exp\left[-\frac{q(\phi_{PF} - \sqrt{q\xi/\pi\epsilon_0\epsilon_S^h})}{kT}\right] \quad (11)$$

where  $\phi_{PF}$  is the electron emission energy from the trap and  $\epsilon_S^h$  is the relative dielectric permittivity at high frequencies. The 1D-VRH model describes a thermal activation current transport from the metal into the semiconductor occurring along the defect states related with a threading dislocation near or below the Fermi level [47]. The conductivity of the device is given by [136]

$$\sigma = \sigma_0 \exp[-(T_0/T)^{0.5}] \quad (12)$$

where  $T_0$  is the characteristic temperature. When TAT is dominant, the reverse current is expressed as follows [137]

$$J \propto \exp\left(\frac{-8\pi\sqrt{2qm_e}}{3h\xi}\phi_T^{3/2}\right) \quad (13)$$

where  $\phi_T$  is the electron trap energy. The strong electric field within the depletion region reduces the lateral distance between the traps and the available states in the

conduction band, substantially increasing the probability of electron tunneling [137]. Figure 9 shows the schematic band diagram of possible reverse leakage current transport mechanisms in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes.

Zhou et al. demonstrated in Pt/ $(\bar{2}01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky contacts that the reverse leakage current is governed by the PF emission with the trap emission energy of  $\sim 0.7 \text{ eV}$  [134]. Yang et al. showed in lateral Pt/ $(\bar{2}01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes that two models including the TAT and 1D-VRH play important roles in the reverse leakage current [47]. Xu et al. reported in Ni/ $(\bar{2}01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky contacts that the TFE and TAT models are dominant at low and high reverse biases, respectively, associated with the deep-level traps at the MS interface [138]. According to the comparative analysis on the Pt/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky contacts

on  $(\bar{2} 01)$  and  $(010)$  substrates, Fu et al. showed that the reverse current for both samples were explained by the TAT and 1D-VRH models [21].

Lingaparthi et al. observed high reverse leakage current in Ni/(001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes [77]. Based on the comparison between experimental and simulation data, they concluded that the thin surface barrier formed by high density of oxygen vacancies near the surface caused tunneling to occur easily. Further, they could reduce the leakage current after annealing in an oxidative environment. Xu et al. showed in Au/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based metal–semiconductor-metal solar blind photodetectors that the dark reverse leakage current is dominated by the TFE at low electric field and the PF emission from a deep trap level of 0.42 eV at high field, respectively [139]. Xia et al. found in Ni/(001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes that the reverse leakage current showed a good fit to the TFE model when the reverse voltage was less than 80 V, and it was dominated by the tunneling effect at higher voltage [67]. They also observed that at high reverse voltage, a large number of electrons are injected into the drift region, and the current follows a trap-assisted space-charge-limited conduction (SCLC) mechanism. Li et al. analyzed the reverse leakage current of Ni/ $(\bar{2} 01)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes using the numerical reverse leakage model [45]. As shown in Fig. 10(a), they could explain the reverse leakage current, with including both the image-force lowering (IFL) and doping effects. They also observed that the linearity in the FN plot shown in Fig. 10(b) deviated with the temperature, indicating that not FE but TFE is strongly involved. Furthermore, they observed that the barrier height from the reverse leakage model is consistent with those from the forward  $I$ – $V$  and  $C$ – $V$  methods. Based on the analysis, they suggested the possibility of achieving the intrinsic breakdown electric field in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes with a high barrier height of 2.2~3 eV, without developing p-n homojunction in Ga<sub>2</sub>O<sub>3</sub> [45]. To data, however, the analysis on the reverse leakage current in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes is limited in the literature. Therefore, the development of various  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based devices requires to clarify the exact transport mechanisms in metal/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> contacts.

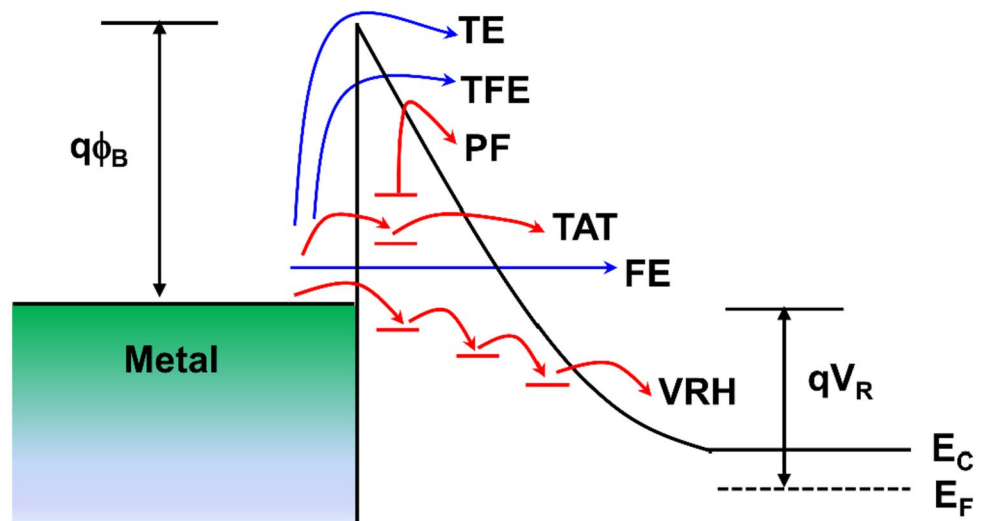
Using CF<sub>4</sub> plasma treatment, Luo et al. reported the suppression of reverse leakage current by four orders of magnitude in Ni/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes [140]. Okumura and Tanaka performed wet and dry etchings for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and investigated various acid and alkali solutions to remove the plasma-induced damage [141]. By immersing the plasma etched samples in hot phosphoric acid solution, they could find the differential on resistance and the ideality factor of (001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes with mesa

termination to be 0.91 m $\Omega$ cm<sup>-2</sup> and 1.03, respectively, and could explain the reverse current by TFE model. Xia et al. comparatively investigated the effects of downstream plasma exposure with O<sub>2</sub>, N<sub>2</sub> and CF<sub>4</sub> on (001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrate and observed that the changes are much less than caused by exposure to hydrogen-containing plasmas [142]. While fabricating Ga<sub>2</sub>O<sub>3</sub> based devices, plasma treatments are used in deep etching for patterning, surface cleaning, resist/dielectric layer removing. In those cases, the plasma-induced damage is unavoidable, which degrades the device performance [48, 58, 143, 144]. Thus, an additional process for minimizing the plasma-induced surface damage is crucial to realize suitable device performance. Yang et al. employed thermal annealing at 450 °C to remove the near-surface damage caused by inductively coupled plasma (ICP) discharges of BCl<sub>3</sub>/Ar [145]. To reduce the surface damage of dry etched  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, Lee et al. performed the wet etching processes using tetramethyl ammonium hydroxide (TMAH) solution and sulfuric peroxide mixture (SPM) solution [146]. Tang et al. reported high performance  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> trench Schottky diodes with the employment of a novel etching technique called self-reactive etching (SRE) [147]. These works suggest that the development of etching and the post etching methods is another important issue in fabricating  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based devices.

Because the thermal stability is critical in the performance of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based devices, the temperature-dependent  $I$ – $V$  measurements were mainly performed at elevated temperatures [42, 50, 72, 78, 79, 87]. But this does not provide full information about the conduction mechanism and the properties of the barrier formation. The low-temperature dependent  $I$ – $V$  characteristics enable us to understand the different aspects of the transport mechanisms. For instances, Reddy et al. investigated the current characteristics of Au/Ni/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes in the temperature range of 100~400 K [65]. Sheoran et al. also characterized the  $I$ – $V$  properties of Au/Ni/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes in the temperature range of 78~350 K [74]. For both works, higher ideality factor than unity at low temperatures was explained by the inhomogeneous Schottky barrier. Meanwhile, Labeled et al. examined the  $I$ – $V$  characteristics of Ni/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky contacts in the temperature range of 100~300 K and concluded that tunneling is reduced while TE is increased with increasing temperature [148]. At low temperatures, tunneling effect becomes more significant in the current conduction [23]. However, there is little research on the low temperature electrical characterization [57, 149], which needs to be considered for future works.



**Fig. 9** Schematic band diagram of possible reverse leakage current transport mechanisms in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes



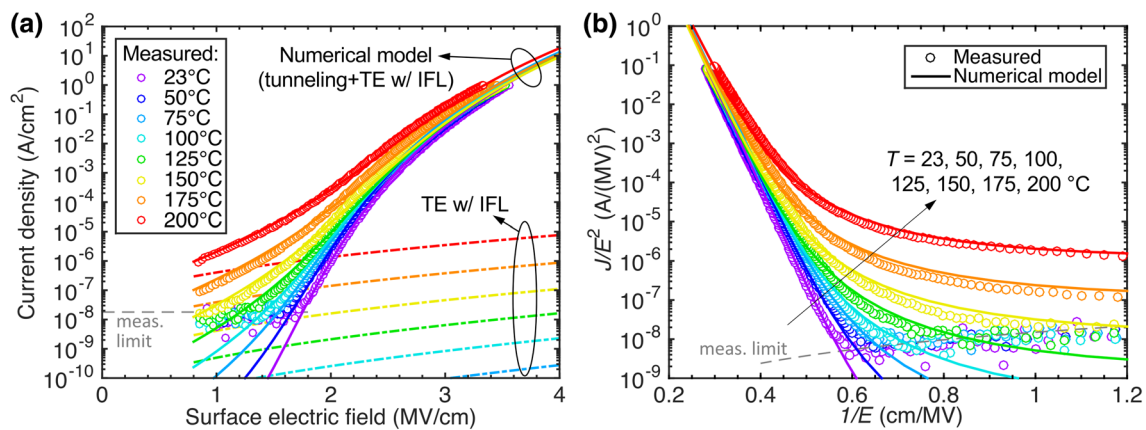
## 6 Surface and deep-level defects in $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

Because the density of surface/interface states plays an important role in determining the effective SBH, passivating these states is essential to improve the diode performance. Therefore, the nature of surface electronic behavior is also an important factor for metal contacts and gas sensing devices. In n-type semiconductors, the FL is pinned at the charge neutrality level (CNL) at the surface due to surface states, in which the surface barrier height is given by [150]

$$q\phi_B = E_g - E_V \quad (14)$$

where  $E_V$  is the valence band maximum (VBM) measured with respect to the FL. Using X-ray photoemission spectroscopy (XPS) measurements, Fu et al. obtained the surface barrier heights of 1.14 and 1.63 eV for the  $(\bar{2}01)$  and  $(010)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> surfaces, respectively. The conduction bands were bent upward, implying the presence of negatively charged surface states and defects near the surfaces [21]. CNL is located near the middle of the band gap in conventional semiconductors such as Si and GaAs, where the metal induced gap states (MIGS) change from a donor-like to an acceptor-like nature [151, 152]. As shown in Fig. 11, the CNLs for ZnO, CdO, In<sub>2</sub>O<sub>3</sub>, and SnO<sub>2</sub> are located at 0.5, 0.4, 0.7, and 0.6 eV above the conduction band minimum (CBM), respectively, which can be understood by the relatively low energy of CBM formed by the low-lying metal s orbitals [153]. Therefore, the surface states tend to be positively charged donor-like, causing electrons to be accumulated near the surface and a downward band bending is observed. The CNL for Ga<sub>2</sub>O<sub>3</sub> is located at 0.6 eV below the CBM, causing both surface electron depletion and upward band bending [154].

Hong et al. performed post deposition annealing at 200 °C for Ni/Au Schottky contacts to  $(001)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrate and found the lower interface trap density and higher reverse breakdown voltage compared to the as-grown sample, which was explained by the NiO formation due to the Ni diffusion into Ga<sub>2</sub>O<sub>3</sub> [155]. Hu et al. employed a floating metal ring (FMR) edge termination structure in Ni/Au contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and found that the interface trap density was in the range of  $1.24 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$  to  $1.71 \times 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$  [80]. Yatskiv et al. investigated the electrical properties of graphite/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky junctions formed on two different  $(\bar{2}01)$  and  $(010)$   $\beta$ -Ga<sub>2</sub>O<sub>3</sub> orientations and found better diode performance for  $(\bar{2}01)$  orientation, associated with a lower density of interface states and their shorter trapping/detrapping time constants [156]. Ingebrigtsen et al. observed the lower reverse leakage current and the lower ideality factor in the  $(010)$  samples compared to the  $(\bar{2}01)$  ones. Using deep level transient spectroscopy (DLTS), they found that the E2 concentration ( $E_C - 0.82 \text{ eV}$ ) in the  $(\bar{2}01)$  samples is higher compared to that in the  $(010)$  samples, associated with the different band bending at the two  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> surfaces [157]. The barrier heights of the oxidized Schottky contacts were 0.5 ~ 0.8 eV higher than their plain metal counterparts, associated with the passivation of interfacial oxygen vacancies and an increase in the work function of the oxidized metals [56]. With the oxygen annealing, Lingparthi et al. observed the passivation of surface states and the reduction of the net carrier concentration, lowering the reverse leakage of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes [158]. These results indicate that the surface/interface states affect the electrical properties of metal/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> contacts and the passivation effect of these states would be investigated further.



**Fig. 10** **a** Temperature-dependent reverse leakage current density, with the numerical reverse leakage model. The contribution from thermionic emission (TE) with image force lowering (IFL) is also

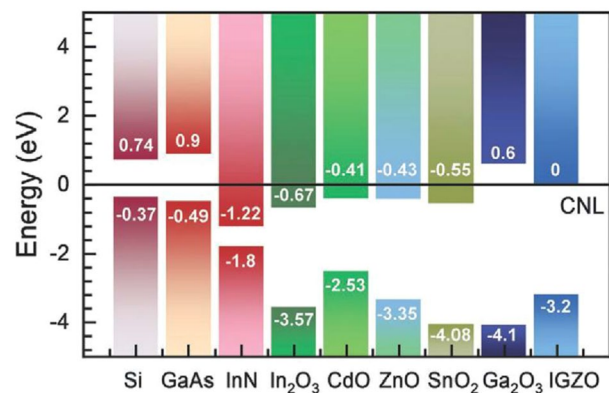
shown. **b** Fowler–Nordheim (FN) plot with the fitting results using the numerical reverse leakage model [45]

Using DLTS and deep-level optical spectroscopy (DLOS) measurements, Zhang et al. investigated the deep-level defects in EFG-grown (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [159]. They reported that the three traps at  $E_C$ -0.62, 0.82, and 1.00 eV are similar to traps in CZ-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> observed by Irmischer et al. [160]. It was predicted that Sn on Ga sites (Sn<sub>Ga</sub>) or oxygen vacancy may be related with the defects at  $E_C$ -0.82 eV [159, 161]. According to the temperature-dependent van der Pauw and Hall-effect measurements for the samples grown by various methods, including EFG, CZ, MBE, and low-pressure chemical vapor deposition (LPCVD), Neal et al. reported that the donor energy of Si and Ge is 30 meV, while the acceptor energies for Fe and Mg are 860 meV and 1.1 eV, respectively [162]. Farzana et al. reported in Ge-doped (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> grown by plasma assisted MBE that the dominant deep-level states are in the middle and lower half parts of the bandgap, with the highest concentration for energy levels at  $E_C$ -2.00 eV,  $E_C$ -3.25 eV, and  $E_C$ -4.37 eV [163]. This is contrary to the results reporting much higher concentrations of defects within the upper bandgap region [159, 160]. Figures 12(a) and (b) show the summary of the energy distribution of deep level defects for EFG-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (010) substrate and Ge-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (010) MBE epitaxial layers, respectively, by Farzana et al. [163]. Very low concentration of relatively shallow levels in the range of  $E_C$ -0.1 eV to  $E_C$ -0.2 eV was observed in PAMBE-grown Ge-doped (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> epitaxial layers, suggesting high potential for future devices where defect levels in the upper regions are responsible for device degradation mechanisms.

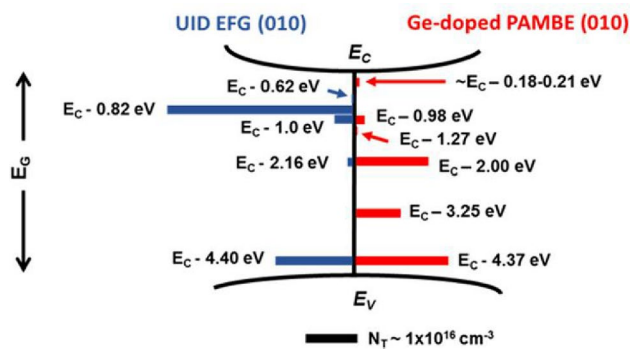
Studies on irradiated samples is also beneficial for identifying and explaining electrically active defects. Ingebrigtsen et al. investigated the impact of proton

irradiation on the charge carrier concentration and electrically active defects [164]. Polyakov et al. investigated the effect of hydrogen plasma on deep-level spectra and suggested that hydrogen plasma exposure could produce surface damage in the near-surface region and compensate shallow donors [165]. Ghadi et al. investigated the deep-level defects in metal organic chemical vapor deposition (MOCVD)-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [166]. As a p-type dopant, Mg acceptor levels in MOCVD-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has also been investigated [167]. According to the growth methods, there may exist various deep-level defects in the epitaxial Ga<sub>2</sub>O<sub>3</sub> layer. As comprehensively reviewed by Wang et al. [168] and Tadjer et al. [169], the origin of deep-level defects is an important electrical component to be studied. These defects can act as electron traps, affecting the current conduction significantly.

Chen et al. investigated the emission kinetics of a single-trap in ( $\bar{2}$  01)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes and reported



**Fig. 11** Band lineups of oxide semiconductors and other conventional semiconductors [153]



**Fig. 12** Summary of the distribution (energy levels and concentrations) of deep-level defects for **a** EFG-grown (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> substrate and **b** MBE-grown Ge-doped (010)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> epitaxial layers. The horizontal bars represent the concentration of each trap state, drawn to the scale of  $1 \times 10^{16} \text{ cm}^{-3}$  as indicated by the black line ( $N_T$ ) [163]

that the deep level E1 ( $E_C - 0.63 \text{ eV}$ ) observed by DLTS is related with the PF emission [170]. Based on the temperature-dependent Hall-effect measurements, Oishi et al. found that the dominant scattering mechanisms are ionized impurity and optical phonon scatterings for the low- and high-temperature regions, respectively [171]. Gong et al. fabricated  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky diodes terminated with p-NiO field limiting rings and reported that the reverse leakage mechanism is identified to be PF emission through localized traps with an energy level of  $E_C - 0.72 \text{ eV}$  [172], similar to the energy level of gallium vacancies ( $V_{\text{Ga}}$ ) in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> determined by DLTS method [173]. Armstrong et al. observed the strong photoconductive gain in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Schottky photodiodes and associated it with self-trapped hole formation near the Schottky diode, lowering the effective Schottky barrier in reverse bias and producing photoconductive gain [174]. Qian et al. employed fluorine plasma treatment in Ga<sub>2</sub>O<sub>3</sub>-based solar-blind photodetectors and found the enhanced device performance due to the passivation of local oxygen vacancies and the suppression of surface chemisorption [175]. However, the detailed mechanism explaining the effect of each defect on the current transport mechanisms is unsatisfactory. Therefore, clarifying the correlation between surface/deep level-defects and current transport mechanisms more thoroughly is suggested for another future work.

## 7 Summary

Many published review papers regarding  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals in the literature are roughly categorized as follows: 1) growth and material properties of bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

[168, 169, 176–181], bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-based power/photonic devices [8, 9, 182–185] and their combination [1, 186–190]. Studies on metal contacts are essential to understand the electrical behavior of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-based devices and the material properties of Ga<sub>2</sub>O<sub>3</sub>. To date, reviews of metal contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals are still lacking [191, 192]. This review suggests the following further research for metal/ $\beta$ -Ga<sub>2</sub>O<sub>3</sub> contacts: (1) clarifying the correlation between various defects and current transport mechanisms based on the temperature-dependent electrical properties, (2) nanoscale electrical investigation to explain the macroscale electrical properties, (3) controllable n-type heavy doping and thermally stable metallization for ohmic contacts. Resultantly, the importance of studies on the metal contacts to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (both bulk and epitaxial layers) will increase continuously.

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## Declarations

**Conflict of interest** The author declares that there is no conflict of interest.

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