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Investigation of Different Metals as Ohmic Contacts to β-Ga_2O_3: Comparison and Analysis of Electrical Behavior, Morphology, and Other Physical Properties

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Nine metals (Ti, In, Ag, Sn, W, Mo, Sc, Zn, and Zr) have been investigated as electrical contacts to *n*-type single-crystal β-Ga_2O_3 substrates as a function of annealing temperature up to 800°C (in flowing Ar). For each contact metal, we investigated its electrical behavior and morphology at each annealing temperature, as well as the effects of adding a Au capping layer. Select metals displayed either ohmic (Ti and In) or pseudo-ohmic (Ag, Sn, and Zr) behavior under certain conditions; however, the morphology was often a problem. It was concluded that metal work function is not a dominant factor in forming an ohmic contact to β-Ga_2O_3 and that limited interfacial reactions play an important role.

Key words: Ohmic metal contacts, gallium oxide, wide bandgap, semiconductor, electrical behavior, morphology

INTRODUCTION

Gallium oxide (Ga_2O_3) has received notable attention as a promising next-generation wide-bandgap semiconductor for a variety of applications, including ultrahigh-efficiency electronics[1–6] and solar-blind ultraviolet (UV) photodetectors.[7–11] β-Ga_2O_3, which is considered the most stable of the five known polytypes of Ga_2O_3, has a bandgap of ~4.8 eV[12–16] and is commercially available as single-crystal substrates produced from the melt.[17] The large bandgap of β-Ga_2O_3 allows it to handle large electric fields, which in turn gives it a Baliga's figure-of-merit (BFoM) for power devices that is 10 and 4 times larger than that of SiC and GaN, respectively.[18,19]

However, because research on wide-bandgap semiconductor devices based on β-Ga_2O_3 is in its very early stages, there is little understanding of how to control device-relevant interfaces to this material. For development of useful Ga_2O_3-based devices, it will be critical to control the properties of electrical contacts. There are several problems pertaining to Ga_2O_3 contacts, such as adherence, electrical instability, and high contact resistance. In this study, we investigated nine different metals as potential ohmic contacts to β-Ga_2O_3, and characterized their electrical behavior and morphology as a function of annealing temperature. The metals were selected based on properties such as work function, melting temperature, and oxide stability. Results of this systematic and comparative study are reported, along with the observed trends and our perspectives.

EXPERIMENTAL PROCEDURES

All substrates used in this work were pieces cut from a 2-inch-diameter, *n*-type β-Ga_2O_3 wafer purchased from Tamura Corporation, Japan. The substrates were grown with Sn as an *in situ* dopant at a concentration of 5×10^{18} cm^{-3}. Prior to metal deposition, each substrate was first degreased by sequentially sonicating in acetone, isopropanol, and deionized (DI) water. It was then soaked in 10% hydrochloric acid (HCl) for 5 min, rinsed in DI water, soaked in boiling hydrogen peroxide (H_2O_2) at 85°C, rinsed again in DI water, and blown dry in nitrogen.

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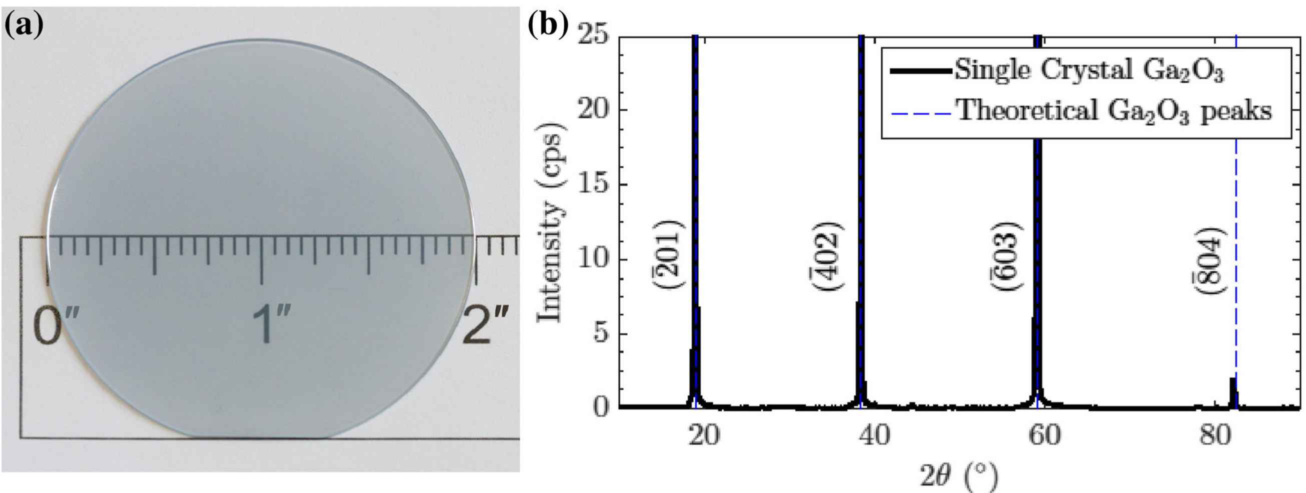


Fig. 1. (a) Photograph and (b) XRD θ–2θ scan of Sn-doped β-Ga_2O_3 wafer.

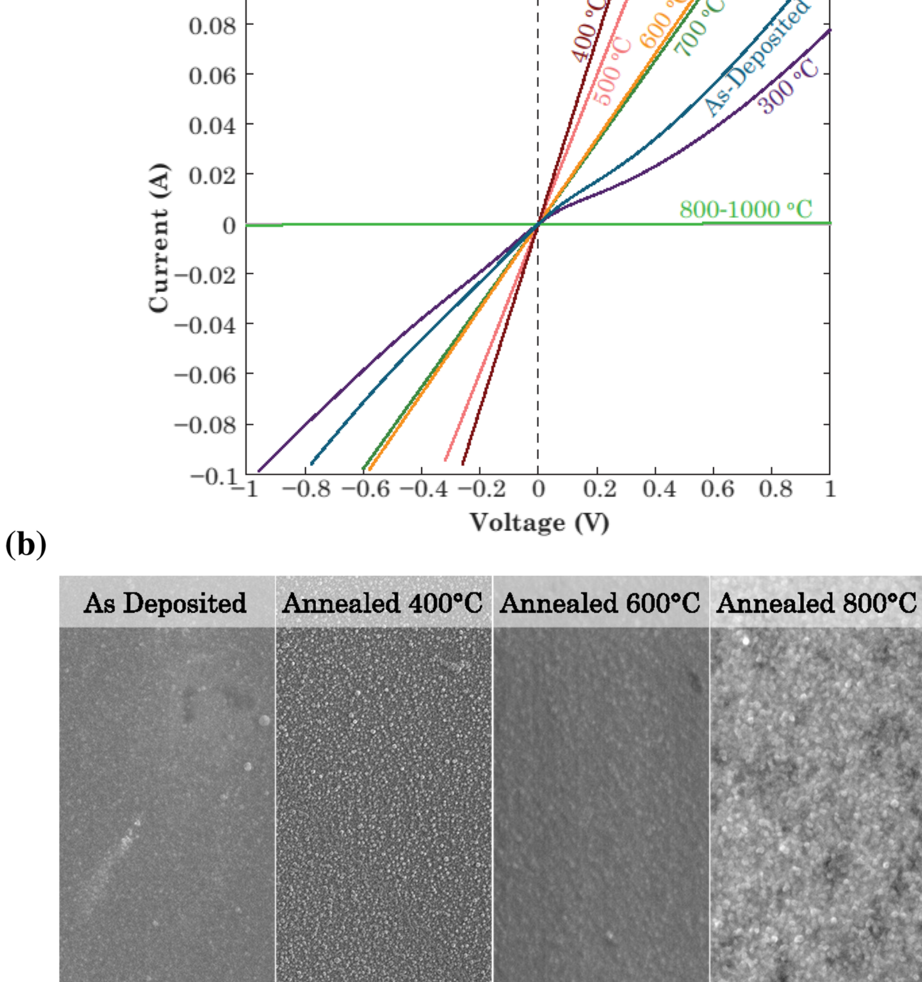
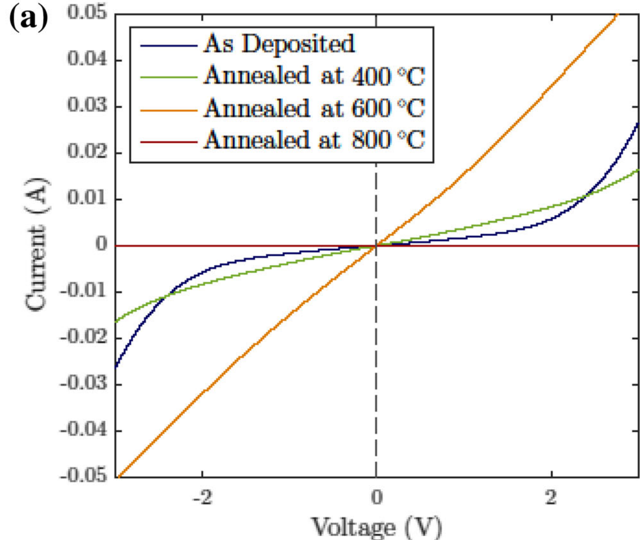


Fig. 2. (a) I–V plots for Ti/Au and (b) SEM images of (bare) Ti on Sn-doped $(\bar{2}01)$ Ga_2O_3 wafer as function of annealing temperature in Ar (annealing time 1 min).



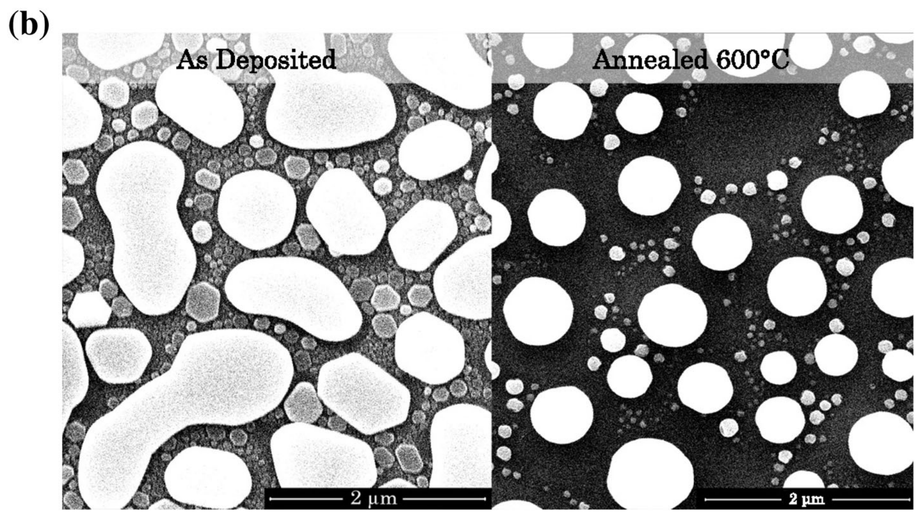


Fig. 3. (a) *I–V* curves and (b) SEM images of morphology of 20-nm-thick as-deposited (left figure) and annealed (600°C for 1 min) (right figure) In contacts on Ga_2O_3.

Each metal was deposited through a shadow mask (500-μm-diameter holes) on an unheated substrate using electron-beam evaporation (base pressure 1×10^{-9} torr to 5×10^{-9} torr) from elemental sources. The purities of the metal sources were as follows: Ti (99.995%), In (99.99%), Ag (99.99%), Sn (99.9999%), Mo (99.98%), W (99.98%), Zr (grade 702), Zn (99.99%), Sc (99.9%). For all metals, both bare (20 nm thick) and Au-coated (100 nm) metal films were deposited and characterized before and after annealing. Anneals were performed in a quartz tube in a resistively heated furnace at 400°C to 800°C in flowing Ar.

Current–voltage (*I–V*) measurements were performed with two probes on adjacent contacts (spacing 500 μm) using an HP 4155B semiconductor parameter analyzer and a Signatone S-1060H-4QR probe station. Scanning electron microscopy (SEM) images were acquired using a FEI Quanta 600 FEG at 15 keV. Energy-dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD) were conducted using an Oxford INCA XMAX 80 mm SDD EDX detector and a PANalytical X'PertPRO MPD x-ray diffractometer, respectively.

RESULTS

Figure 1a shows a photo of the 2-inch-diameter, Sn-doped β-Ga_2O_3 wafer prior to dicing. The slight color tint is attributed to Sn dopant impurities. The θ–2θ XRD spectrum in Fig. 1b shows primary peaks from the set of $\{\bar{2}01\}$ diffraction planes, confirming the $<\bar{2}01>$ orientation of the crystal. Hall measurements indicated that the crystal had *n*-type conductivity with resistivity of 0.025 Ω cm, electron mobility of 50 $cm^2\ V^{-1}\ s^{-1}$, and free electron concentration of $5 \times 10^{18}\ cm^{-3}$.

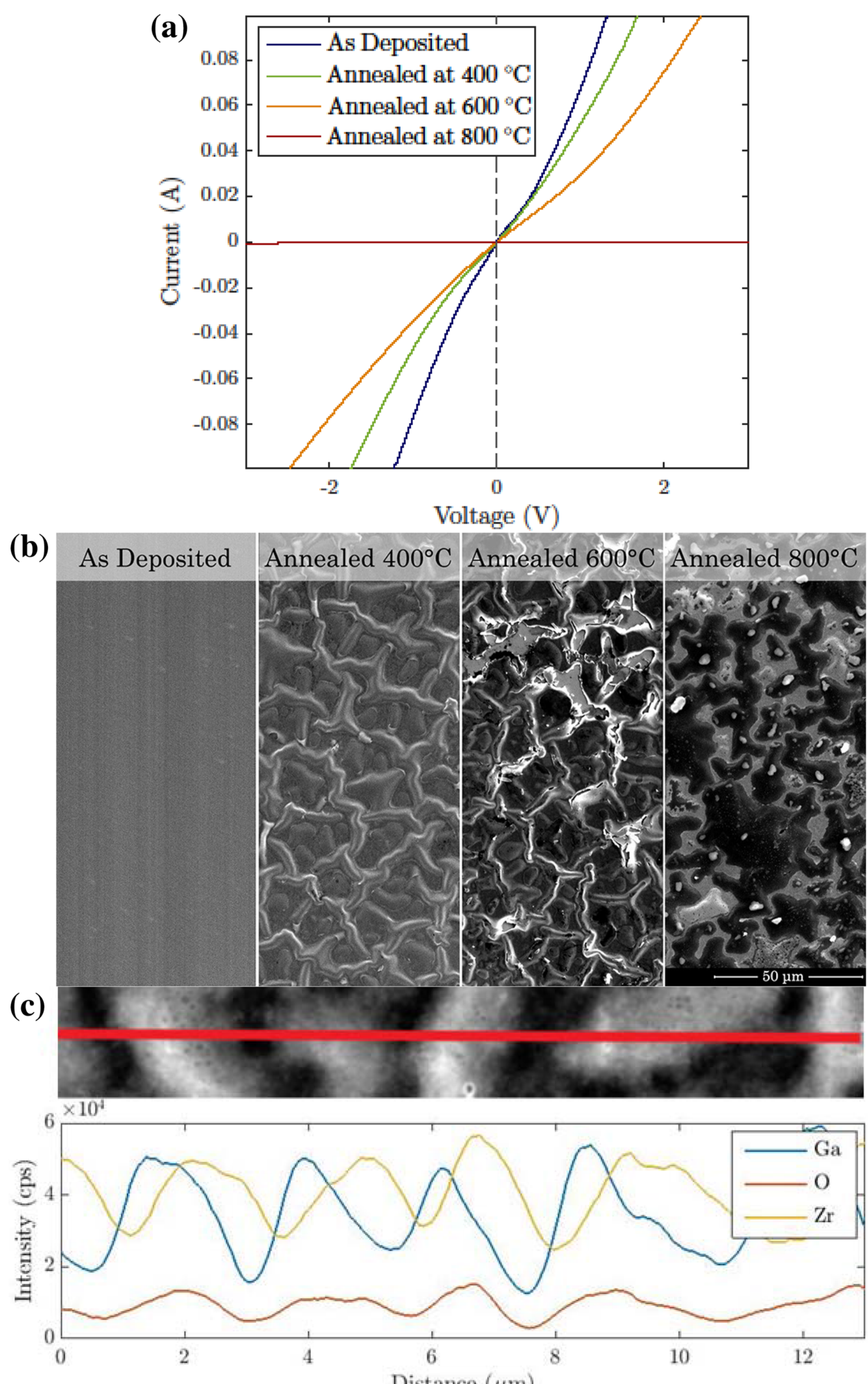


Fig. 4. (a) *I–V* curves of Zr/Au contacts, and (b) SEM of (bare) Zr contacts after annealing at indicated temperatures. (c) EDX intensity profiles of Ga, Zr, and O acquired along the red line across the Zr/Ga_2O_3 topography after annealing at 600°C (Color figure online).

The Ga_2O_3 wafer was diced into smaller pieces for the metal contact investigations. The pieces were cleaned immediately prior to each metal deposition as described above.

Ti/Au has been commonly reported as an ohmic contact metal for Ga_2O_3-based devices.[2–6,8,9] We conducted an annealing series (between 300°C and 900°C for 1 min at each temperature) for Ti/Au (20 nm/100 nm) contacts on Ga_2O_3 to investigate whether there is an optimal annealing temperature. As shown in the *I–V* plots in Fig. 2a, the lowest resistivity was obtained after annealing at 400°C.

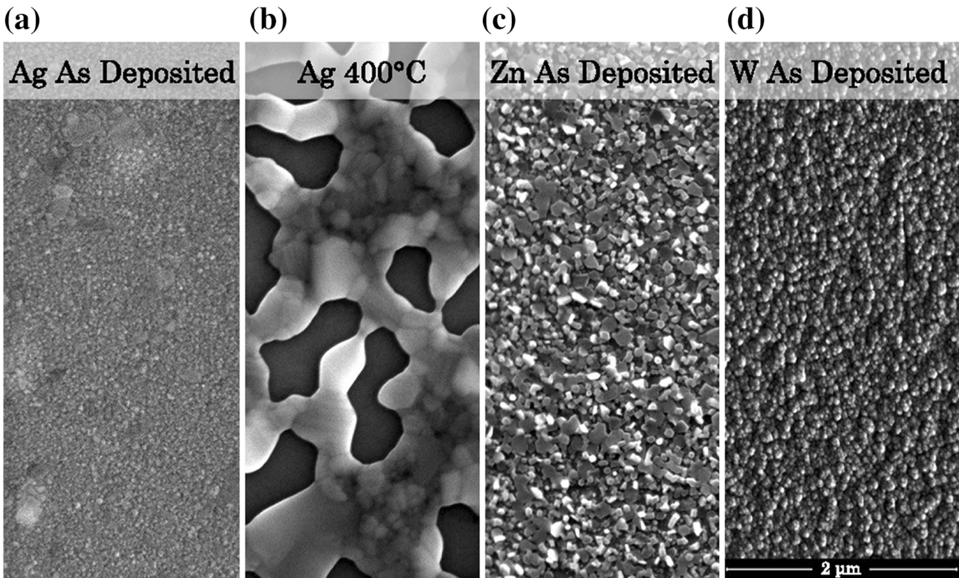


Fig. 5. SEM images of (a) Ag as deposited, (b) Ag after 400°C anneal, (c) Zn as deposited, and (d) W as deposited. Scale bar in (d) applies to all images.

The contacts deteriorated when annealed above 500°C. Figure 2b shows that Ti/Ga_2O_3 contacts maintained a continuous, smooth morphology throughout the annealing series.

Although Ti readily forms an ohmic contact to Ga_2O_3, Ti is not thermodynamically stable with Ga_2O_3. The free energies of formation of Ti oxides are more negative than that of Ga_2O_3, which indicates that Ti will reduce Ga_2O_3, possibly forming an insulating oxide layer at the interface, given sufficient time at elevated temperature. This phenomenon likely causes the degraded electrical behavior for annealing temperatures $>500°C$. It would therefore be desirable to have alternative choices for metals to use as ohmic contacts.

One approach to form ohmic contacts is to reduce the Schottky barrier height (SBH) at the metal–semiconductor interface. Schottky–Mott theory predicts that the SBH (Φ_B) equals the difference between the electron affinity of the semiconductor (χ_S) and the work function of the metal (Φ_M)[20]:

$$\Phi_B = \Phi_M - \chi_S. \tag{1}$$

Based on a reported electron affinity of 3.5 eV to 3.7 eV for Ga_2O_3 on GaN,[21] one might expect that metals having work functions of $\sim$3.7 eV or less would form ohmic contacts. High doping concentration in the semiconductor should enable ohmic contacts to be formed from metals with somewhat higher work functions. For most transition metals, $\Phi_M > 4.0$ eV.

Indium was an initial metal of interest, as it has a relatively low Φ_M (4.1 eV) and, based on thermodynamics, should not reduce gallium oxide. As shown in Fig. 3a, In contacts became ohmic after annealing at 600°C for 1 min, in agreement with results of another study.[22] Although In contacts have shown some usefulness as ohmic contacts, they are not very practical due to the low melting point of In; these contacts dewet the Ga_2O_3 surface in the as-deposited condition, and melt during the ohmic contact anneal (Fig. 3b). Furthermore, use of an Au capping layer on the In contacts did not result in improved morphology or electrical behavior, either with or without annealing.

We also investigated two metals, Sc and Zr, that have lower work function than Ti or In. Interestingly, although Sc (Φ_M = 3.5 eV) has one of the lowest work functions of all transition metals, it did not display ohmic behavior either before or after annealing at temperatures up to 800°C. Its morphology (not shown) was similar to Ti. Because Sc is a strong oxide former, one might expect a Au capping layer to result in improved electrical behavior. Although addition of a Au capping layer did yield contacts with lower resistivity, Sc/Au contacts also did not display ohmic behavior before or after annealing.

Zirconium sits directly below Ti in the Periodic Table. With its low Φ_M (4.05 eV) and chemical similarity to Ti, we expected Zr to readily form an ohmic contact to Ga_2O_3. As in the case of Ti, the Zr contacts also displayed improved electrical behavior (lower resistivity) with a Au capping layer. Zr/Au contacts also displayed pseudo-ohmic behavior in the as-deposited condition (Fig. 4a). However, the contacts continually degraded with increasing annealing temperature, unlike Ti/Au contacts, which showed improved ohmic behavior with moderate (400°C to 500°C) annealing. We attribute the cause of this degradation to reduction of the Ga_2O_3 by Zr to form

Table I. Properties and observed behavior of metals investigated as contacts to Sn-doped β-Ga_2O_3

Metal	Φ_M (eV)[24]	Melting point (°C)	Stability of oxide (relative to Ga_2O_3)	Possible intermetallic phases[25]	Morphology	Ohmic?	Conditions, if ohmic/pseudo-ohmic
Sc	3.5	1541	More stable	Ga_3Sc, Ga_2Sc, GaSc, Ga_4Sc_5, Ga_3Sc_5	Continuous, smooth	No	–
Zr	4.05	1855	More stable	Ga_3Zr, Ga_2Zr, Ga_5Zr_3, Ga_3Zr_2, Ga_2Zr_3, Ga_3Zr_5, $GaZr_2$	Continuous, smooth as deposited/ rough after anneal	Pseudo	As deposited only (Zr/Au)
In	4.1	157	Less stable	–	Dewets	Yes	600°C, 1 min anneal
Ag	4.26	962	Less stable	–	Dewets	Pseudo	As deposited
Zn	4.3	420	Comparable, depends on temperature	–	Continuous, rough (plate-like)	No	–
Ti	4.33	1668	More stable	Ti_3Ga, Ti_2Ga, Ti_5Ga_3, Ti_5Ga_4, TiGa, Ti_2Ga_3, Ti_3Ga_5, $TiGa_2$, $TiGa_3$	Continuous, smooth	Yes	400°C to 500°C, 1 min anneal
Sn	4.42	232	Less stable	–	Dewets	Pseudo	As deposited
W	4.55	3422	Less stable	–	Continuous	No	–
Mo	4.6	2623	Less stable	Mo_3Ga, MoGa, $MoGa_2$, Mo_6Ga_{31}, Mo_8Ga_{41}	Continuous	No	–

free Ga plus Zr oxide. The free energy of formation for ZrO_2 ($\Delta G_f = -1019$ kJ mol^{-1} at 400°C) is more negative than that of either Ga_2O_3 ($\Delta G_f = -640$ kJ mol^{-1} at 400°C) or TiO_2 ($\Delta G_f = -870$ kJ mol^{-1} at 400°C), indicating a stronger driving force for Zr oxide formation. Our SEM and EDX analyses (Fig. 4b and c) of (bare) Zr/Ga_2O_3 contacts supported this conclusion. Specifically, SEM images showed that a continuous, smooth morphology in the as-deposited condition became rough after the 400°C anneal, and showed evidence for a melted and resolidified phase after the 600°C anneal. EDX elemental profiles (Fig. 4c) along a randomly selected line from the 600°C annealed sample showed fluctuations in intensities for Ga, Zr, and O. Also, the peak intensities for Zr and O were approximately co-located and offset from the locations for the Ga peak intensities. This result indicates that reduction of Ga_2O_3 by Zr to form Ga and Zr oxide occurred during the annealing process.

Tin was also investigated as a potential ohmic contact metal, as it is an *n*-type dopant in Ga_2O_3 and yields transparent conducting films with conductivity up to at least 38 Ω^{-1} cm^{-1}.[23] However, Sn contacts were found to dewet Ga_2O_3, both in the as-deposited condition and after annealing, having a morphology (not shown) that appeared similar to the In contacts. An Au capping layer did not significantly affect the morphology. Although Sn and Sn/Au formed pseudo-ohmic contacts in the as-deposited condition, the electrical behavior degraded upon annealing.

Ag and Ag/Au contacts displayed electrical behavior similar to Sn and Sn/Au. Interestingly, Ag and Ag/Au contacts appeared to form continuous films in the as-deposited condition, but dewetted the Ga_2O_3 surface upon annealing, as shown in Fig. 5a and b.

The results for the metal contacts discussed above, along with three other metals that did not form ohmic contacts (Zn, W, and Mo), are summarized in Table I. Although Zn has a Φ_M that is nearly the same as that of Ti, Zn and Zn/Au contacts did not show ohmic behavior under any conditions; they became increasingly resistive with increasing annealing temperature. As shown in Fig. 5c, the contacts appeared continuous but had a rough (plate-like) morphology.

W and Mo were also investigated to extend the range of work functions included. These two metals also have very high melting points and less stable oxides than Ga_2O_3. The morphologies of these contacts were similar to each other and remained continuous throughout the annealing series; the morphology of an as-deposited W contact is shown in Fig. 5d as an example. W, W/Au, Mo, and Mo/Au contacts did not display ohmic behavior either before or after annealing up to 800°C.

DISCUSSION

This study indicates that there are a number of complex factors involved in formation of ohmic

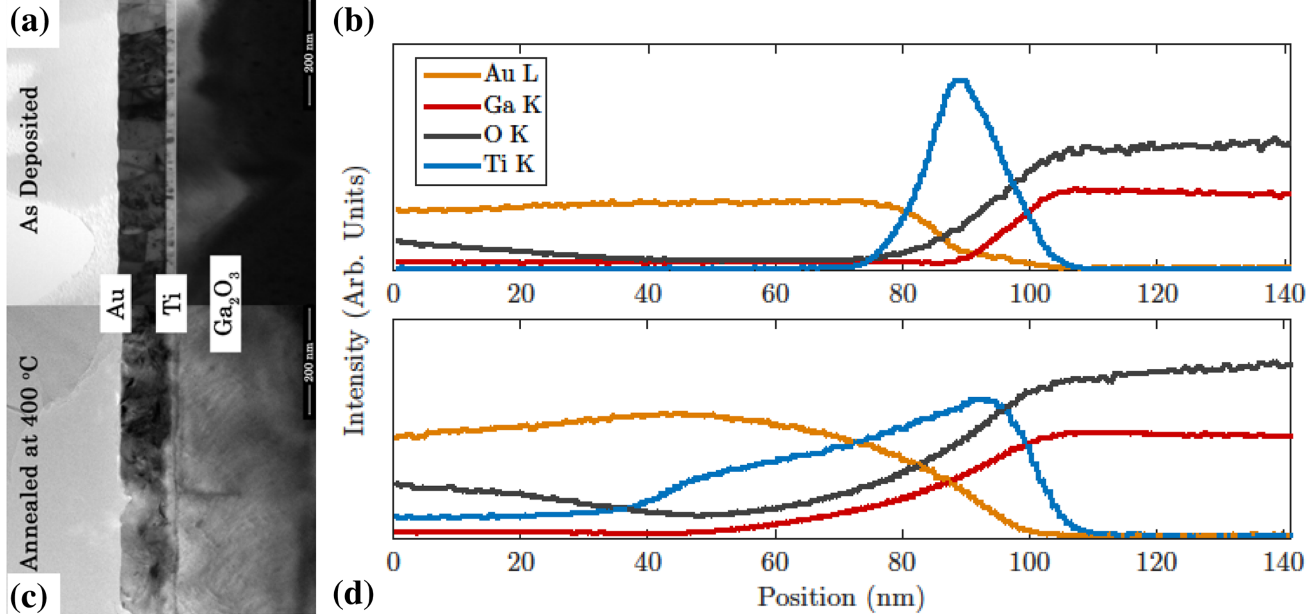


Fig. 6. (a, c) Cross-section TEM micrographs and (b, d) EDX line profiles of Ti/Au contact on Ga_2O_3 as deposited and after annealing at 400°C, as indicated.

contacts to n-type (Sn-doped) β-Ga_2O_3 substrates. The results of this study specifically pertain to ($\bar{2}$01)-oriented β-Ga_2O_3 substrates treated with HCl and H_2O_2 prior to metal deposition by electron beam evaporation.

Firstly, it is apparent that the work function of the metal is not a dominant factor determining whether it forms an ohmic contact to these substrates. In particular, Sc, which has a very low Φ_M, did not form an ohmic contact even with a Au capping layer, which should help prevent oxidation of the underlying Sc metal layer.

Secondly, there is evidence that interfacial reaction—in limited amount—plays an important role in formation of ohmic contacts to Ga_2O_3. Titanium, which has a more stable oxide than Ga_2O_3, reacts with the Ga_2O_3 substrate to form ohmic contacts after annealing at 400°C. Cross-sectional transmission electron microscopy (TEM) and EDX of Ti/Au contacts showed interdiffusion of Ga and O into the Ti layer (Fig. 6). However, too much reaction, as observed for Zr/Au contacts annealed at $T \geq 400$°C and Ti/Au contacts annealed at $T > 500$°C, resulted in contact degradation characterized by an increase in resistance.

This study also shows that morphology is a problem for many metals on Ga_2O_3. This is not too surprising, considering that oxides tend to have low surface energy. However, interestingly, the metals with lowest surface energy (In, Ag, and Sn) dewetted the surface, which is opposite to what would be expected. Therefore, the strength of interfacial bonding between the metal and Ga_2O_3 likely determines whether the metal dewets or forms a continuous film. We note that the metals that have significant chemical affinity (i.e., higher oxide stability and/or possibility for intermetallic compounds) with Ga_2O_3 formed continuous films, whereas the metals that have low chemical affinity (i.e., lower oxide stability and no intermetallic compounds) with Ga_2O_3 were observed to dewet the surface. The only exception to this trend is W, which formed a continuous film even though it does not appear to have significant chemical affinity for Ga_2O_3. One possible reason for this behavior may be low atom mobility, associated with tungsten's very high melting point.

CONCLUSIONS

We investigated the electrical behavior and morphology of nine contact metals (Ti, In, Ag, Sn, W, Mo, Sc, Zn, and Zr) to n-type single-crystal β-Ga_2O_3 substrates. We found that Ti contacts with a Au capping layer were ohmic with the lowest resistance after annealing at 400°C for 1 min. However, the contacts degraded when annealed above 500°C. Indium displayed ohmic behavior after annealing to 600°C but suffered from poor morphology. Whereas Ag, Sn, and Zr displayed pseudo-ohmic behavior in the as-deposited condition, morphology tended to be an issue for these contacts, especially when annealed. Sc, Mo, and W did not display ohmic behavior before or after annealing up to 800°C.

In summary, we found that formation of ohmic contacts to β-Ga_2O_3 is not determined by any one dominant factor, such as metal work function, and that limited interfacial reactions play an important role in both the morphology and electrical behavior. Further work is needed to investigate optimized metal stacks and processing conditions to achieve

thermally stable ohmic contacts having low contact resistance and suitable morphology.

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