Transactions on Computer Science and Intelligent Systems Research
ISSN: 2960-1800, eISSN: 2960-2238 | Volume 7
TPCEE 2024

Transformation From Schottky to Ohmic Contact at High Temperature in Diamond Schottky Barrier Diode

Shuning Cui *

School of Energy and Electrical Engineering, Chang'an University, Xi'an, China

* Corresponding Author Email: 2022906224@chd.edu.cn

Abstract. Relations between Schottky contact and ohmic contact in diamond Schottky diode is attentively studied. Whether the metal-semiconductor contact forms metal carbide at high temperature on the interface of p-diamond is showed to determine the character of the contact. Formation of carbide and/or intermixing of metal and p-diamond at elevated temperature are believed to lower the Schottky barrier height and make Schottky contact "ohimicize" in a certain extent. This transformation can be advantageous for fabricating ideal ohmic contact, especially when boosted by annealing, but it can also be detrimental to maintaining high-quality Schottky contact at higher temperature. This suggests general criteria for identifying potential candidates for the two types of contact. Oxide and/or surface intermixture formed by metal and Oxygen-Terminals (OTs) on p-diamond, however, can resist the transformation trend at high temperature, thereby leading to better thermal stability. Nevertheless, the desorption of OTs at certain temperature may lead to re-reaction between metal and carbon, thus lowering the barrier again. Luckily, this temperature limit for certain metal is usually higher than the operating high-enough temperature and has less to do with the thermal stability and effectiveness of the functioning diode. Finally, careful selection of metal materials combined with adjustment of Schottky barrier height through high temperature can help fabricate desirable, robust and more economic diamond Schottky diode working at required higher temperature. Similar phenomenon may be observed for non-diamond Schottky diode as well and further researches can be conducted.

Keywords: Diamond Schottky diode; Schottky barrier height; Schottky contact.

1. Introduction

Diamond has been studied for long to be applied as electronics operating at high temperature, high power, high frequency and other extreme environment due to its wide bandgap (5.47 eV), high natural thermal conductivity (22 W/cm · K), high breakdown field (10 MV/cm), high electron and hole mobility (especially for CVD diamond, 4500 $cm^2/V \cdot s$ and 3800 $cm^2/V \cdot s$) and high electron and hole saturation velocity (2×10^7 cm/s and 0.8×10^7 cm/s) (all room temperature) [1]. Diamond Schottky diode, as a rectifying passive device working with majority carriers capable of operating at high frequency and high temperature environment, is one of diamond's significant applications as semiconductor material, though some technical problems still exist such as less controllable doping concentration and accuracy. With the development of CVD growth techniques and breakthroughs on p-doping diamond crystal, researches on Diamond Schottky Barrier Diode based on Boron-doped p-diamond have been carried out in a large scale. It is noticed that hyper temperature may lead to interface "reaction" (whether chemical or physical depends) between metal and diamond, leading to an increase in reverse leakage current and poorer rectification property. It is also acknowledged that good ohmic contact on the other part of the device (whether vertical, pseudo-vertical, or transverse structure) can be formed mainly through high temperature annealing to change the interface. The possible reasons for each have been discussed and analyzed by many researchers, but there seems to be a lack of a comprehensive overview and a careful comparison. Therefore, further observation is conducted on the relationships between Schottky contact and ohmic contact especially at elevated temperature. Some ideas concerning the transformation of the two contacts at high temperature are recognized, while different characteristics between different materials also make a difference. General principles of the transformation are raised and many examples and/or anti-examples are found and demonstrated, while general strict mathematical models are still under research and some of the interface mechanisms are still waiting to be explored. The principles provide a general and potential way of searching for possible candidates to form either thermal stable Schottky contact or ohmic contact in desirable I-V (Current-Voltage) linearity. The principles also fit well in adjusting the Schottky contact to make it more ohmic ("ohmicize"), which can be applied to fabricate diamond Schottky diodes operating at high temperature with less consumption of forward power, adding economy. Oxygen-Terminals (OTs) on p-diamond are revealed to play a crucial role as well. The following sections will primarily consist of discussions and examples.

2. Discussions and Examples

2.1. Discussion and Comparison

The latest research progress of Diamond Schottky Barrier Diode is summarized and introduced by Peng Bo's [2]. Through careful comparison, concerning the determination of materials to form ohmic contact and Schottky contact, a certain extent of complementarity is found, but some specific issues still need to be discussed and analyze specifically. Furthermore, detailed examples are found and illustrated. P-diamond doped by Boron is mainly discussed.

Due to the fact that ohmic contact requires the contact resistance to be as small as possible, high concentration doping is usually applied to diamond before metal-semiconductor contact to lower the width of barrier region and enhance tunnelling current dramatically. Meanwhile, the formation of metal carbide on the interface is also used to promote a more linear I-V character. The reason is that metal carbide between metal and highly-doped p-diamond can help reduce the barrier on the interface, thereby lowering the resistance. Hence, searching for metal or alloy that can form carbide with diamond may help explore potential candidates for ohmic contact such as Ti, whose barrier was determined to be (0.63 ± 0.13) eV on p-type diamond (001), and Ta with a contact resistivity of $5.3\times10^{-5}\ \Omega\cdot\mathrm{cm}^2$ in TaSi/Au systems [3, 4].

What is more worthy of noticing is that high temperature annealing during fabrication of ohmic contact can help form carbide phases, creating a layer full of active defects for lower barrier height and increasing leakage current. This helps none or poor ohmic metal contact "ohmicize" and boosts conventional ohmic contact. For instance, it was notably reported that W/p-diamond, who has no ohmic character or interface carbide at 300°C, can perform linear I-V behavior after annealing at more than 400°C with a resulting contact resistance of $8.2\times10^{-4}\ \Omega\cdot\mathrm{cm}^2$ and a barrier height decreasing from (1.16 ± 0.14) eV (300°C) to (0.45 ± 0.14) eV at 500°C [5]. The reason was indicated to be the formation of tungsten carbide (WC) on the interface at elevated temperature. Moreover, similar reasons exist causing decrease of barrier height at high annealing temperature in cases like Ti and Pd [6-8]. Even Au which is special for its extreme chemical stability was found such property. Specifically, although no reaction was observed between Au and p-diamond before and after annealing, contact resistance was still reported to decline after annealing ascribed to the enhanced intermixing of C and Au resulting in a thin intermediate carbon layer rich in Au [9]. As a result, appearance of carbide or carbon-mixed layer after high temperature annealing may be a crucial factor of fabricating high quality ohmic contact. Conversely, Pd forms no carbide with Hydrogen Terminals (HTs) p-diamond after annealing, making annealing less useful to improve its ohmic character (though already pretty good with Schottky barrier height of (-0.15 ± 0.1) eV before annealing) [8].

On the other hand, an ideal rectifying Schottky contact aims for better thermal stability of high Schottky barrier height under extreme temperature. However, forming a carbide on the interface for leakage current means a less ideal high Schottky barrier height. Therefore, considering ideal Schottky contact, the material applied should form no carbide on the interface especially at high temperature without annealing so as to hinder the transformation from Schottky contact to ohmic one and lift thermal stability. Some of the counter-examples are Al, whose Schottky barrier height decreases drastically at about 575K and Cr with a considerably lower height (mainly less than 1 eV) (depicted in Fig.1). That is mostly due to interface additional mechanism related to carbide beyond carrier thermionic emission, as was discussed [10]. A good example of Ni will be demonstrated later.

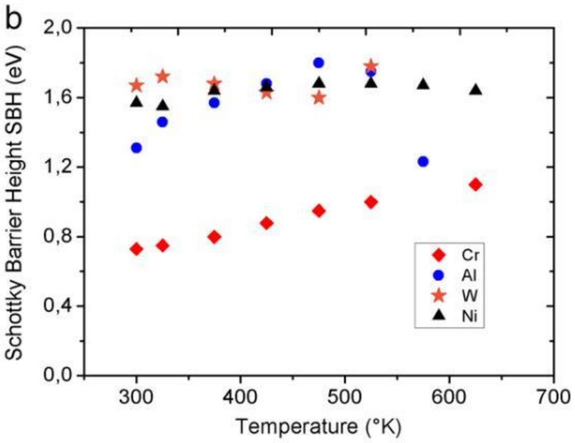

Figure 1. The Schottky Barrier Height (SBH) for W, Al,
Cr and Ni Schottky contact to diamond as functions of temperature [10].

What is worth emphasizing here is that the thermal stability of Schottky barrier is also partly susceptible to the interface reaction or intermixing of metal and Oxygen Terminals (OTs) on p-diamond, resembling the Metal-Oxide-Semiconductor (MOS) structure. This leads to the formation of oxide intermediate layer that resists possible desorption of OTs to become CO or CO2 at high temperature (over 470°C), preventing barrier decline, thus maintaining thermal stability of the Schottky contact [11]. A vivid counter-example is that because Au has no further reaction with OTs diamond, heating at 870K will cause a reduction of OTs and a consequent change of electronic states on the interface. This can reduce its Schottky barrier height at 300K from 2.2 eV to 1.1 eV irreversibly [12]. Among many, Zr/OTs diamond possesses high thermal stability even after 723K annealing (Schottky barrier height still 1eV remaining) owing to the accumulation of Oxygen forming a thin, homogeneous oxide layer on the interface (depicted in Fig.2 (d)) [13]. In a nutshell, it is suggested to look for materials forming nearly no carbide at high temperature and further being capable of reacting with OTs and forming oxide, whether thick or thin, on the interface of p-diamond to ensure high thermal stability of desirable Schottky barrier.

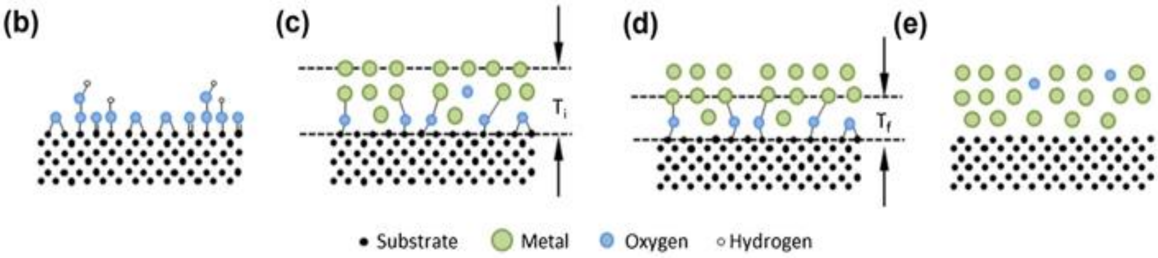

Figure 2. Schematic model of the OTs diamond interface versus thermal treatment: (b) after the diamond-surface VUV/ozone treatment, (c) after metal deposition, (d) annealed, (e) annealed till oxygen desorption. (Ti,f) refer to initial and final thickness (0.5nm and 0.2nm, respectively) [13].

Moreover, the annealing for further ohmic contact and the application of oxidation process for more stable Schottky contact can be applied together, allowing us to adjust the barrier height within a certain scale at high temperature so as to either find potential candidate for ohmic contact or lower the height of Schottky barrier height to a certain extent, thus lowering forward power lost of Schottky diode to make it more economic. For example, Zr/OTs diamond Schottky barrier height switches from above 2 eV (obvious Schottky contact due to oxide) to around 1 eV ("ohmicized" by annealing) at about 450°C and remains stable up to 500°C, as was demonstrated, although the principles behind this (when oxide meets annealing) are quite complicated and different factors are usually intertwined together [14].

2.2. Examples and Applications

With appropriate alternation and careful material selecting, the Schottky diode can be made effective and economic while maintaining excellent thermal stability at relatively higher temperature.

A list of comprehensive examples is described as follows. A pseudo-vertical diamond Schottky diode with Ni/Au Schottky contact was reported to operate at 473K in 2017 [15]. Ni shows an insignificant reaction with diamond and forms no interface carbide, resulting in a Schottky barrier height of 1.57 eV (Fig.1), a high rectifying factor of 10^{10} and great thermal stability within the scope of 300K-625K [10]. Au covering Ni is used to avoid non-interfacial oxidation at high temperature. Cu/OTs p-diamond Schottky diodes working at elevated temperature were fabricated for the first time in 2015 to become a promising high-power, high-temperature-operating device, in which Cu-Schottky was deposed on OTs B-doped p-diamond and Cu/Ti electrodes were evaporated and annealed at 600°C to form ohmic contact as well [16]. The diode demonstrated extraordinary stable I-V character at about 400°C and possessed a Schottky barrier height of about 1.6 eV unchanged after annealing, achieving a high rectification ration of about 10^5 at 800°C. The switch from Cu-Schottky to Cu-Ohmic was supposed to be owing to the interfacial reaction and/or interdiffusion of Cu and diamond when OTs on diamond surface begins to dissociate after about 500°C and culminates at 600°C. Therefore, owing to the fact that the Oxygen related desorption temperature (about 500°C) is considerably higher than the stable Schottky barrier temperature (400°C), the Schottky diode will be still perfect when applied to automobiles engines operating at 100-300°C, ensuring its effectiveness. Ag/OTs p-diamond diode fabricated by K.Ueda's in 2012 also manifested high rectification ratio at the magnitude of 10^4 at high temperature (600°C) , which was even better than Ni who showed no typical rectification above 600°C in their study [17]. The material selection was said due to the fact that either Ag or Ni have no reaction with diamond below 1000°C. However, the leakage current of Ag/p-diamond diode increases above 600°C and the difference also increases as temperature goes upwards and the diode finally loses its rectification over 800°C. The reason was speculated to be the similar interfacial reaction and/or interdiffusion between Ag and diamond film.

Because the OTs desorption temperature is usually higher than the operation temperature (which is usually high enough for sufficient application) of metal (e.g. Cu, Ag) /OTs p-diamond, OTs forming oxide can still act effectively at work to resist desorption and maintain high Schottky barrier height of the diode. This ensures the thermal stability and provokes the idea that for a higher working temperature, finding more robust oxide formation material can be an option.

3. Conclusion

In diamond Schottky barrier diode, the formation of carbide and/or intermixture of metal and p-diamond at elevated temperature contributes to lowering the Schottky barrier height and make Schottky contact less ideal in a certain extent. This transformation, referred to as "ohmicize", indicates certain degree of switching from Schottky contact to ohmic contact at high temperature, measured by Schottky barrier height or resistivity. This can be advantageous for fabricating ideal ohmic contact with great I-V linearity, especially if boosted by annealing during fabrication of the electrodes. The process, meanwhile, means no more stable Schottky barrier height at high temperature, which is detrimental to ensuring high-quality and high-thermal-stability diode. This contradictory character infers possible general criteria of finding potential candidates for the two contacts, simply speaking, "non-carbide forming" for basis of Schottky contact and "carbide forming" for ohmic one at elevated temperature. An additional criterion for high thermal stability Schottky contact is the existence of oxide and/or surface intermixture formed by metal and Oxygen-Terminals (OTs) on p-diamond. Such intermediate layer, despite of thickness, can resist the desorption of OTs and the transformation trend when temperature goes upwards, thereby leading to better thermal stability with large rectifying factor. Nonetheless, the dissociation of OTs into CO and CO2 after certain temperature (much higher) may lead to re-reaction of metal and carbon and some other complicated interface mechanisms, thus lowering the barrier. Luckily, this temperature limit for some material is usually higher than the functioning relatively-high temperature and has little influence on the thermal stability and rectification capability of the diode. Finally, careful selection of metal materials, including testing and judging the interfacial product compounds of both contacts and the OTs desorption temperature for Schottky contact, along with adjusting Schottky barrier height through high-temperature annealing can help fabricate a thermally stable, rectifying, robust, and economic diamond Schottky diode that operates at required higher temperatures. Since diamond is special for extreme properties, similar interface phenomenon and consequences may exist for non-diamond Schottky diode as well and further researches can be conducted.

This research clarifies the possible routines of selecting potential materials and adjusting them for better diamond Schottky diode. The idea can be possibly expended and applied to ways of choosing materials for non-diamond Schottky contact and ohmic contact. Further experiments can be carried out for testification and theoretical research on elaborating the mechanisms within the layer and unifying the models are good directions in the future.

References

[1] C. J. H. Wort, R. S. Balmer, Diamond as an electronic material, Materials Today 11 (2008) 22-28.

[2] P. Bo, L. Qi, J. Shumiao, F. Shuwei, W. Ruozheng, W. Hongxing, Research Progress of Diamond Schottky Barrier Diodes, Journal of Synthetic Crystals 52(5) (2023).

[3] S. Kono, T. Teraji, H. Kodama, K. Ichikawa, S. Ohnishi, A. Sawabe, Direct determination of the barrier height of Ti-based ohmic contact on p-type diamond (001), Diamond and Related Materials 60 (2015) 117-122.

[4] K. Das, V. Venkatesan, T. P. Humphreys, Ohmic contacts on diamond by B ion implantation and TiC-Au and TaSi2-Au metallization, J. Appl. Phys. 76(1994) 2208-2212.

[5] D. Zhao et al., Effects of rapid thermal annealing on the contact of tungsten/p-diamond, Appl. Surf. Sci. 443 (2018) 361-366.

[6] T. Tachibana, B. E. Williams, J. T. Glass, Correlation of the electrical properties of metal contacts on diamond films with the chemical nature of the metal-diamond interface. II. Titanium contacts: A carbide-forming metal, Phys. Rev. B 45 (1992) 11975-11981.

[7] Y. Wang et al., Ohmic contacts and interface properties of Au/Ti/p-diamond prepared by r.f. sputtering, Surf. Interface Anal. 29 (2000) 478-481.

[8] W. Wang et al., Palladium Ohmic contact on hydrogen-terminated single crystal diamond film, Diamond and Related Materials 59 (2015) 90-94.

[9] C. M. Zhen, X. Q. Wang, X. C. Wu, C. X. Liu, D. L. Hou, Au/p-diamond ohmic contacts deposited by RF sputtering, Appl. Surf. Sci. 255 (2008) 2916-2919.

[10] S. Koné et al., An assessment of contact metallization for high power and high temperature diamond Schottky devices, Diamond and Related Materials 27–28 (2012) 23-28.

[11] T. Teraji, Y. Garino, Y. Koide, T. Ito, Low-leakage p-type diamond Schottky diodes prepared using vacuum ultraviolet light/ozone treatment, J. Appl. Phys. 105 (2009) 126109.

[12] T. Teraji, Y. Koide, T. Ito, High-temperature stability of Au/p-type diamond Schottky diode, Physica Rapid Research Ltrs 3 (2009) 211-213.

[13] J. C. Piñero et al., Atomic composition of WC/ and Zr/O-terminated diamond Schottky interfaces close to ideality, Appl. Surf. Sci. 395 (2017) 200-207.

[14] A. Traoré, P. Muret, A. Fiori, D. Eon, E. Gheeraert, J. Pernot, Zr/oxidized diamond interface for high power Schottky diodes, Appl. Phys. Lett. 104 (2014) 052105.

[15] R. Monflier et al., Diamond Schottky diodes operating at 473 K, EPE Journal 27 (2017) 118-124.

[16] K. Ueda, K. Kawamoto, H. Asano, High-temperature and high-voltage characteristics of Cu/diamond Schottky diodes, Diamond and Related Materials 57 (2015) 28-31.

[17] K. Ueda, K. Kawamoto, T. Soumiya, H. Asano, High-temperature characteristics of Ag and Ni/diamond Schottky diodes, Diamond and Related Materials 38 (2013) 41-44.