Solid-State Electronics 185 (2021) 108152

Contents lists available at ScienceDirect

Solid State Electronics

journal homepage: www.elsevier.com/locate/sse

Improved interface characteristics of Mo/4H-SiC schottky contact

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A R T I C L E I N F O

The review of this paper was arranged by S. Cristoloveanu

Keywords:
4H-SiC
Schottky interface
Schottky barrier height

A B S T R A C T

In this work, we studied different proportions of Mo-C alloy Schottky contacts. Compare the electrical characteristics and SiC interface with the Mo/4H-SiC based diodes. The Schottky interface obtained was studied at different annealing temperatures and its electrical properties were analyzed. Analyze electrical performance through temperature-related current–voltage (I-V) and capacitance–voltage (C-V) measurements. The experimental results showed that the metallic Mo-C alloy (9:1) Schottky contact had good stability and interface characteristics at high annealing temperatures. When annealing at 900 °C, its ideality factor approached 1 and the barrier height reached 1.04 eV. The TEM images also indicated that the Mo-C alloy reduced the solid-state reaction, which improved the inhomogeneity of the Schottky interface.

1. Introduction

Silicon carbide (SiC) semiconductor materials have been developed in the fields of high temperature, high frequency, high pressure, high power and low power consumption due to its advantages [1–4]. However, the metal/semiconductor contact has been a key problem that needs to be solved in the manufacture of silicon carbide devices for a long time [5–7]. This means that silicon carbide Schottky contacts are required to perform better in electrical properties, such as obtaining a stable ideality factor, high barrier height and lower reverse leakage current [8–12]. A large number of studies have shown that [13–17], metal–semiconductor Schottky contacts are the key to improving reliability and stability of silicon carbide devices. The performance of silicon carbide depends largely on the quality of the metal/semiconductor contact. Therefore, the stability and practicality of silicon carbide devices lies in the formation of excellent Schottky contacts [18–20]. After the Schottky contact is made, a rapid thermal annealing process can be adopted for the structure. During the annealing process, the dangling bonds of the Schottky contact interface will be removed [21–23].

In recent years, the studies have reported the use of metallic molybdenum (Mo) as the Schottky contact metal of SiC [24–27]. Based on the properties of Mo, like it is less sensitive to thermal budget and provides relatively low Schottky barrier on 4H-SiC. But these studies indicate that the Schottky contact of Mo on n-type 4H-SiC is annealed at different temperatures and found that the Schottky barrier at the interface has serious inhomogeneity [27,28]. This may be due to the irregular arrangement of some free atoms at the Schottky contact interface [26]. In the rapid thermal annealing process, the Schottky deposited metal will undergo a solid state reaction with the semiconductor at the contact interface, resulting in inhomogeneity SiC interface. To explain departures from ideality, Tung's model [41] considers in the presence of locally non-uniform regions or nanometer-size "patches" with relatively lower or higher barriers. The electrical characteristics of Schottky diodes depend to a large extent on the quality of Schottky contacts [29–33]. Moreover, Mo can easily react with Si elements to form silicide, while reacting with C elements can form carbides [34,35]. It is necessary to avoid excessive reaction at the interface between the Schottky deposited metal and the semiconductor material. We choice Mo-C alloy as the Schottky contact metal, adding C to the top metallization. In the rapid thermal annealing process, Mo-C alloy may undergo a solid state reaction and Mo will not participate in the interface reaction of SiC. Therefore it can form a homogeneity Schottky contact barrier and good Schottky interface characteristics.

In this study, we studied two sets of Mo-C alloy Schottky contacts with different ratios and a set of Mo comparison systems. The Mo 4H-SiC comparison system was defined as Group A. The atomic ratio of Mo and C in the Mo-C alloy was set to two different values, where the atomic ratio of Mo and C is 4:1 (group B) and 9:1 (group C), respectively. By analyzing the current–voltage (I-V) and capacitance–voltage (C-V) characteristics of these three groups of structures, some important

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https://doi.org/10.1016/j.sse.2021.108152
Received 30 January 2021; Received in revised form 21 June 2021; Accepted 8 July 2021
Available online 13 July 2021

electrical parameters of Schottky contacts can be determined. The samples were analyzed by transmission electron microscopy (TEM), which proved that the Mo-C alloy system improved the homogeneity of the interface during high temperature annealing.

2. Device fabrication and experiment

The diode was fabricated using a 4H-SiC epitaxial wafer from Cree, Inc. The carrier concentrations of the substrate and epitaxial layers (10.28 μm) were 1.0×10^{18} and 1.22×10^{16} cm^{-3}. The SiC substrate were washed sequentially in acetone, isopropanol and buffered oxide etchant (BOE) prior to metal deposition and blown dry with nitrogen. At the temperature of 1150 °C, SiO_2 (50 nm) was grown on the front by dry oxygen, and then SiO_2 (250 nm) was deposited on the epitaxial layer by plasma enhanced chemical vapor deposition (PECVD) to form plate termination. The length of the SiO_2 FP termination was 20 μm. A 150 nm thick metal Ni was sputter deposited on the backside of the samples and annealed at 950 °C for two minutes in nitrogen to form an ohmic contact. In this experiment, a molybdenum-carbon target with a purity of 99.9% was used, and the molybdenum-carbon atomic ratio was 4:1 and 9:1, respectively. The metal Mo and Mo-C alloy (150 nm) of the same thickness were deposited by radio frequency sputtering to form Schottky contacts, and then a 100 nm Au layer was deposited as the Schottky metal electrode. The effective area of the device (0.196×10^{-2} cm^2) was patterned by the standard dry etching method.

After metal deposition, the SBDs was annealed by rapid thermal annealing in nitrogen atmosphere for one minute. Five annealing temperatures were set, which were 600, 650, 700, 750, 800, 850, 900, 950 and 1000 °C. Using an Agilent B1505A analyzer, Current versus voltage (IV) and capacitance versus voltage (CV) were performed on the Schottky contacts after annealing at different temperatures to evaluate the barrier height ϕ_b and the ideality factor.

3. Experimental results and analysis

The current density versus voltage (J-V) characteristics of the Mo Schottky diodes samples (group A) annealed at different annealing temperatures are shown in Fig. 1.

As shown in Fig. 1, it can be observed that the Schottky device of this structure has reasonable rectification properties as a whole in the forward curve. At the same time, it can be observed that the Schottky contact annealed in the range of 600 °C–850 °C has a single barrier curve. When the annealing temperature is above 900 °C, the silicon carbide diode has an obvious double barrier phenomenon, and there are both a lower Schottky barrier height and a higher Schottky barrier height. And with the increase of annealing temperature, the unevenness of Schottky barrier becomes more and more obvious. According to literature surveys [31], it is known that Mo metal and silicon carbide are highly prone to chemical reactions to form molybdenum carbides and silicide. Obviously, the Schottky interface annealed at 900 °C has formed an alloy (silicide or carbides) layer.

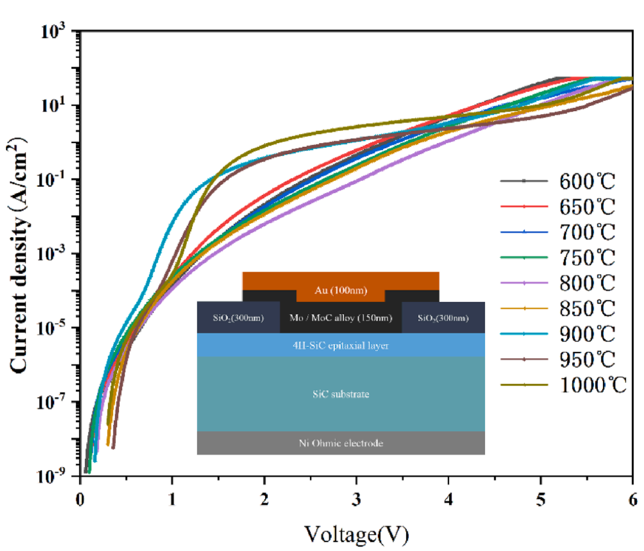

Fig. 1. J-V characteristics of SiC SBDs with Mo electrodes at different annealing temperatures.

The primary mechanism of current transport in wide-bandgap semiconductor materials is thermal electron emission across the barrier, provided the material is lightly doped and the operating temperature is not very low [36]. Thus, the parameters n and ϕ_b can be obtained from the J-V curve as shown in Table 1.

The metal–semiconductor space charge region contact resembles a single-sided abrupt junction. Under reverse bias, the space charge region width increases, and the C-V characteristics of the SBD are typically measured at a reverse voltage [37]. Fig. 2 shows C-V characteristic curves at different values of annealing temperatures.

The barrier heights ϕ_b corresponding to different annealing temperatures and calculated using the $1/C^2$-V curve is shown in Table 1. The ideality factor n is an applicability parameter for the theory of thermionic emission. If tunneling or recombination does not occur, $n = 1$, otherwise $n > 1$. As different materials and processes involved during fabrication may have defects, the Schottky barrier height is inhomogeneous and consequently, the ideality factor generally deviates from the ideal value. It can be seen from Table 1 that the ideality factor of the Mo metal system after annealing in the range of 600 °C–850 °C deviates greatly from the ideal value, which shows that in addition to the thermionic emission mechanism, other transport mechanisms of the Schottky system are also effective plays an important role.

The large ideality factor may be due to defects in the Schottky interface [38,39]. Observing the value of the ideality factor in the table, it can be considered that there are some defects caused by the process steps at the Schottky contact interface. These defects will become recombination centre to assist tunneling current, or form interface states. Although the I-V characteristics of the device deviated from thermionic emission after annealing in this temperature range, the sample still has rectifying characteristics. It can be observed from the table that the barrier height gradually increases as the annealing temperature increases, but due to the excessive ideality factor, it is considered that the system has seriously deviated from the thermionic emission current transport mechanism. So the Schottky barrier calculated is not reliable.

It is observed from Table 1 that although the effective doping concentration N_D of Schottky diodes of group A increases gradually at different annealing temperatures, it can fluctuate in a small range, and is more in line with the actual doping concentration value provided by the SiC substrate (1.22×10^{16} cm^{-3}). This phenomenon indicates that the epitaxial layer doping of the system is relatively uniform. It can be observed from the table that the barrier height extracted using the C-V

Table 1
Contact barriers characteristic parameters of Mo 4H-SiC at different annealing temperatures.

Temperature (°C)	SBH (eV)		Ideality factor	N_D (cm^{-3})
	J-V	C-V		
600	0.97	1.25	1.58	1.24E16
650	0.99	1.26	1.45	1.24E16
700	1.00	1.28	1.25	1.25E16
750	1.00	1.25	1.25	1.25E16
800	1.06	1.30	1.12	1.29E16
850	1.02	1.32	1.44	1.27E16
900	–	1.29	–	1.31E16
950	–	1.29	–	1.30E16
1000	–	1.31	–	1.31E16

Note: "–" means no data.

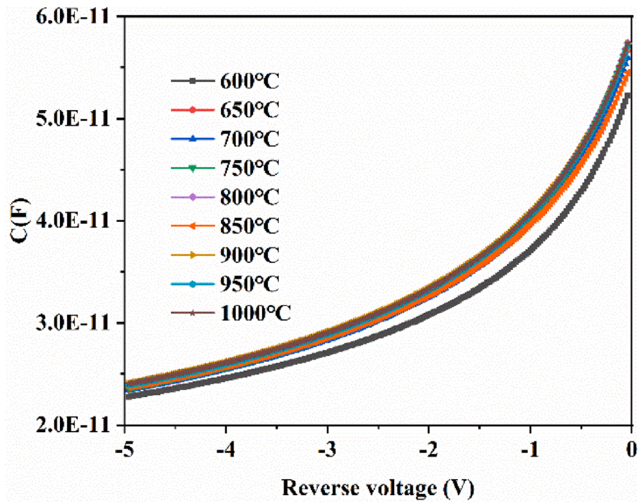

Fig. 2. C-V characteristics curves of SiC SBDs with Mo electrodes at different annealing temperatures.

curve is significantly greater than that extracted using the I-V curve. This difference is usually caused by the local leakage current around the Schottky metal electrode or the uneven composition at the interface. According to the model proposed by Werner and Gutter [40], this difference in barrier height can be explained well. In this model, the metal–semiconductor interface is rough rather than uniform, which is caused by the large fluctuations in the Schottky barrier height. C-V measurement does not involve the current transport mechanism, and naturally does not involve the transmission of free carriers. Due to the inhomogeneity of the interface, the forward current will preferentially flow through the Schottky contact in the region with the lowest barrier height, so I-V measurement will be affected by the low barrier region, and C-V will be more sensitive to the high barrier region. This causes the barrier height obtained from the I-V curve to be significantly lower than that obtained from the C-V curve.

Then, the B group system Mo-C alloy (4:1) and the C group system Mo-C alloy (9:1) 4H-SiC SBD were selected for electrical test analysis. Fig. 3 shows the current density and voltage (JV) characteristics of Schottky diode at different annealing temperatures.

According to Fig. 3(a), it can be observed that the samples of group B exhibited a poor linear curve at 600 °C annealing temperature. This may be due to the incomplete chemical reaction of Mo-C alloy and the silicon carbide interface when annealing at 600 °C There will be a large amount of free C element, which results in a poor interface and an unsmooth positive curve. As the annealing temperature gradually increases from 650 °C, it can be observed that the forward curve gradually shifts to the left, the turn-on voltage is gradually reduced, and the forward curve is relatively smooth, with good rectification characteristics. From Fig. 3 (b), it can be observed that the C group and the first two groups show a smooth positive characteristic curve. With the annealing temperature increasing from 600 °C, it can be observed that the forward curve gradually shifts to the left and the turn-on voltage gradually decreases. It shows that reducing the C content in the Mo-C alloy has a great improvement effect on the positive characteristics. It can be considered that the reduction of the C content in the C group makes the compound reaction of the Mo C alloy more sufficient. It will avoid excessive reaction at the interface between the Schottky deposited metal and the semiconductor material.

Fig. 4 shows the changes in barrier height and ideality factor of SiC SBD at different annealing temperatures. It can be seen from Fig. 4(a) that the ideality factor of the samples of group B after annealing in the range of 650 °C–750 °C deviates greatly from the ideal value. We speculate that there are excess free C elements, which introduce defects on the interface, and these defects introduce recombination centre to

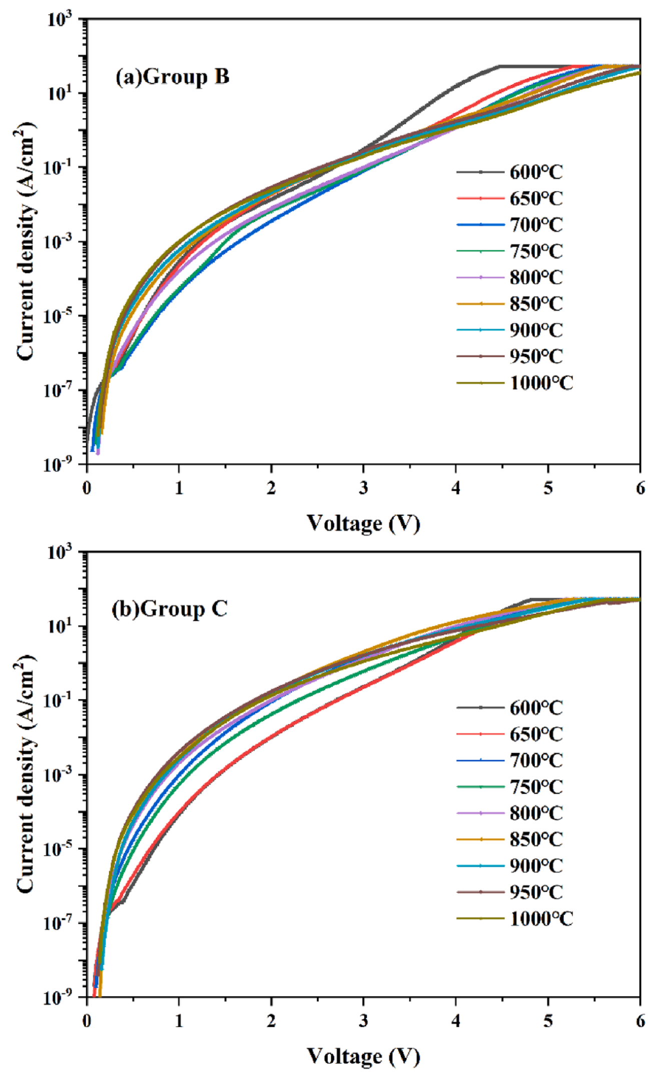

Fig. 3. J-V characteristics of SiC SBDs with Mo-C electrodes at different annealing temperatures.

assist the tunnel current, so that in addition to the thermionic emission mechanism, other transport mechanisms also play an important role. At the same time, it can be observed that the ideality factors of the samples of group B after annealing in the range of 800 °C–1000 °C all approach the ideal value 1. This indicates that the Mo-C alloy may undergo a sufficient chemical reaction under annealing conditions above 800 °C and follows the thermionic emission theory. As the annealing temperature increases, the overall barrier height of Schottky gradually rises to a certain height and then tends to balance, and the overall level remains between 0.9 and 1.1 eV. We have known the samples from A group has an obvious double barrier phenomenon when the annealing temperature is above 900 °C. This shows that the B group samples still have good Schottky barrier homogeneity under high temperature annealing conditions, and have good rectification characteristics, and their electrical properties under high temperature annealing are better than those of group A samples. It is proved that the Mo-C alloy system improves the Schottky interface characteristics under high temperature annealing, and thus has excellent electrical characteristics and stability.

It can be seen from Fig. 4(b) that the ideality factor of the samples of group C after annealing in the range of 650 °C–750 °C is similar to that of samples of group B, and they all deviate greatly from the ideal value. This may be due to the insufficient reaction of the Mo-C alloy in this temperature range. At the same time, it can be observed that the ideality

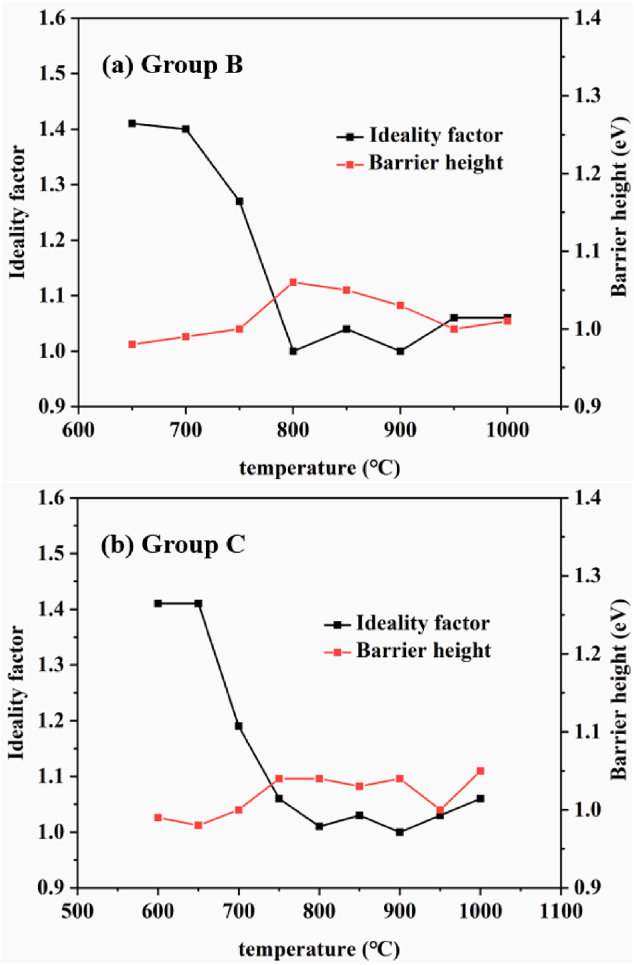

Fig. 4. Changes of barrier height and ideality factor of Mo-C alloy SiC SBD at different annealing temperatures.

factors of the samples of group C annealing in the temperature range of 750 °C–1000 °C are all approaching to the ideal value 1, and the values are relatively stable without much deviation. This shows that under the high temperature annealing condition, the Schottky metal Mo-C alloy of group C has a sufficient compound reaction. And group C showed better electrical characteristics than group B. With the continuous increase of the annealing temperature, the ideality factor tends to the ideal value at the annealing temperature of 750 °C and above, and there is no major change. With the gradual increase of the annealing temperature, the Schottky barrier height is between 0.99 and 1.05 eV, and there is no major change. It can be seen from this that the samples of group C have good interface homogeneity and rectification characteristics under different high-temperature annealing conditions.

Compared with the samples of group A and group B, the samples of group C showed the best electrical properties, as well as the homogeneity and stability of the interface at high annealing temperature. Therefore, improving the content of C in the Mo-C alloy has a very positive effect on Schottky contact. Reducing the content of C element can make the Mo-C alloy more fully undergo compound reaction during the annealing process, reduce the formation of free C element, and greatly improve the homogeneity of the barrier of the interface. It also verified the theory proposed in this article again, that is, it avoids the solid-state reaction of Schottky metal Mo and silicon carbide interface, resulting in the silicon carbide interface not having excessive reaction with metal.

Table 2 shows the barrier heights calculated by different methods for the samples of group B and group C. It can be observed from the table that the two sets of barrier heights calculated by C-V are significantly greater than those calculated by I-V. However, the barrier height calculated by the two methods fluctuates in a smaller range. This shows that the Mo-C alloy system has improved the interface characteristics of Schottky contacts and has a relatively uniform Schottky barrier. Compared with the Mo 4H-SiC SBD system of group A, it can be seen that the homogeneity of the Schottky barrier in the capacitance characteristics of the samples of group B and C is improved, and it shows better Schottky contact interface.

Table 2
Contact barriers characteristic parameters of Mo 4H-SiC at different annealing temperatures.

Temperature (°C)	Group B SBH (eV)		Group C SBH (eV)	
	J-V	C-V	J-V	C-V
600	–	1.50	0.99	1.41
650	0.98	1.26	0.98	1.22
700	0.99	1.24	1.00	1.23
750	1.00	1.22	1.04	1.26
800	1.06	1.24	1.04	1.22
850	1.05	1.24	1.03	1.23
900	1.03	1.21	1.04	1.24
950	1.00	1.22	1.00	1.21
1000	1.01	1.23	1.05	1.23

Note: "–" means no data.

The samples annealed at 900 °C in group A and C were selected, and cross-sectional images of the samples were prepared with focused ion beam. The TEM image of the metal-SiC interface is shown in Fig. 5.

It can be observed from Fig. 5(a) that the silicon carbide interface of this system exhibits poor homogeneity at 900 °C annealing. And it was observed that a white reaction zone formed between the metal Mo and SiC interface. This is due to the solid-state reaction between Mo and SiC interface during the annealing process, and the mutual diffusion of Mo and Si elements. It is confirmed that the interface inhomogeneity of the Mo 4H-SiC SBD basic system will cause the deterioration of Schottky's electrical properties. From the TEM image of Fig. 5(b), it can be observed that at 900 °C annealing, a relatively uniform and smooth Schottky contact interface is formed between the Mo-C alloy metal and the silicon carbide interface. This is because the Mo-C alloy does not excessively react with the silicon carbide interface during the annealing process, so that the homogeneity of the Schottky interface is improved. Therefore, combined with the electrical characteristic analysis of the previous section, it is concluded that the Mo-C alloy Schottky contact under high temperature annealing has better interface homogeneity and electrical characteristics.

4. Conclusion

In this paper, the Schottky contact characteristics of three systems of metal Mo, Mo-C alloy (4:1) and Mo-C alloy (9:1) on n-type 4H-SiC are studied. We choice Mo-C alloy as the Schottky contact metal, it may undergo a solid state reaction and Mo will not participate in the interface reaction of SiC in the rapid thermal annealing process. The results show that the Mo-based system has poor interface characteristics under high temperature annealing, the ideality factor is far greater than the ideal value, and the double barrier phenomenon appears, showing poor electrical characteristics. In contrast, the two Mo C alloy systems exhibit relatively uniform interface characteristics, the ideality factor is also close to 1, and the barrier height does not fluctuate greatly with the annealing temperature, and has good electrical characteristics. Combined with the characterization image analysis, it is proved that the metallic Mo-C alloy (9:1) can greatly improve the Schottky interface and has good Schottky contact potential.

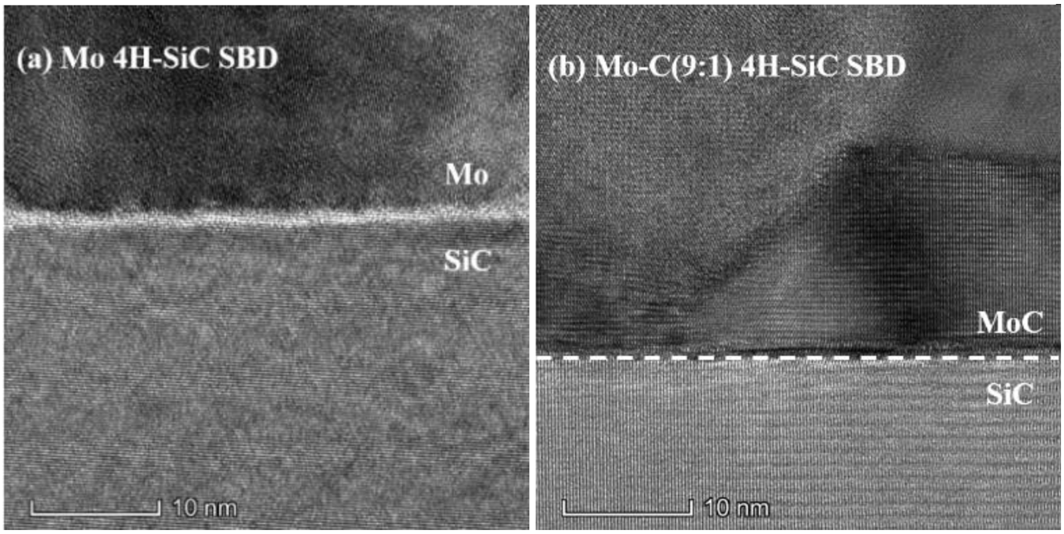

Fig. 5. TEM images of Mo and Mo-C electrodes at annealing temperatures of 900 °C.

CRediT authorship contribution statement

Ke-han Chen: Writing - original draft. **Fei Cao:** Formal analysis. **Zhao-yang Yang:** Writing - review & editing. **Xing-ji Li:** Methodology. **Jian-qun Yang:** Methodology. **Ding-kun Shi:** Data curation. **Ying Wang:** Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported in part by the National Natural Science Foundation of China (No. 61774052, 61904045) and in part by Science and Technology on Analog Integrated Circuit Laboratory (No. 6142802180507).

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