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Direct observation of interfacial reaction of Ni/6H-SiC and carbon redistribution by in situ transmission electron microscopy

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ABSTRACT

The interfacial reaction of Ni/SiC has been attracting considerable attention because SiC substrate has excellent chemical and thermal stability and low electrical resistivity, which are essential properties for various device applications. However, research on the initial reaction at low temperature and exact mechanism is currently insufficient. Therefore, we investigated the reaction of Ni films on a 6H-SiC substrate and the behavior of carbon at 550 °C by direct observation with transmission electron microscopy (TEM) during in situ heating. At 550 °C, the $Ni_{31}Si_{12}$ phase formed during the reaction of Ni and SiC. The Ni silicide layer thickened as the reaction front proceeded toward the 6H-SiC substrate and carbon atoms from decomposed SiC converted into graphite. In addition, carbon existed in three regions. First, carbon existed as graphite on the external surface of Ni silicide layer during initial reaction. Second, graphite formed at the original interface between the Ni film and the 6H-SiC substrate. Finally, carbon existed at the bottom of the Ni silicide region due to its low diffusivity in the silicide. The elemental distribution of Ni, Si, and C was observed in detail through various analytical techniques. We demonstrate the reaction mechanism of Ni and SiC at 550 °C and the distribution of carbon atoms.

1. Introduction

Silicon carbide (SiC) has properties that are more desirable than those of silicon, for instance, its wider band gap, higher mechanical hardness, and excellent thermal conductivity. These properties are advantageous for efficient high-power device operation [1,2]. In the fabrication of SiC-based electronic devices, the formation of the metal/SiC contact (metallization) is one of the most important steps. In particular, Ni/SiC contacts are most commonly used in electronic devices due to their chemical and thermal stability as well as their low electrical resistivity. Most studies of the Ni/SiC reaction have been carried out at high temperatures and for long annealing times [2–5]. Although some results have been reported from various temperatures, the mechanisms underlying the initial reaction and the carbon diffusion behavior are unclear [2,6]. By precisely understanding the reaction through analyzing the microstructural evolution and elemental redistribution, it is possible to control reasonably appropriate variables for fabricating the device.

In a previous work, we analyzed the formation of silicides and the diffusion behavior of carbon during Ni/SiC reactions at low temperatures using rapid thermal annealing (RTA) [7]. At 550 °C, the results show that carbon atoms from the decomposed SiC remained in the reaction zone and precipitated as graphite within the Ni silicide layer. However, all studies thus far, including our previous work, have investigated the microstructure after the reaction and predicted the process (so-called ex situ experiments); thus, in situ experiments are necessary to investigate the reaction process in further detail and to study the kinetics of the Ni/SiC reaction. Although some papers have reported the results of in situ experiments on the Ni/SiC reaction at high temperatures, these studies used X-ray diffractometry (XRD) or angle-resolved synchrotron-radiation X-ray photoemission spectroscopy (SR-XPS), which exhibit difficulties in demonstrating the microstructural evolution and distribution of the phases formed during the reaction [8,9].

Therefore, the present paper is mainly focused on directly observing the Ni/SiC reaction at a low temperature in real time using transmission electron microscopy (TEM) to investigate the exact the mechanism of the Ni/SiC interfacial reaction and the behavior of carbon. In addition, various analytical techniques in TEM were used to investigate the microstructure and distribution of each element and/or phase. Although the critical temperature for the dissociation of SiC was previously determined to be approximately 500 °C [10], we set the target

Abbreviations: TEM, Transmission electron microscopy; NBED, Nano-beam electron diffraction; EDS, Energy dispersive X-ray spectroscopy; EELS, Electron energy loss spectroscopy

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temperature to 550 °C to compare these results with the previous ex situ results.

2. Materials and Methods

The n-type c-face 6H-SiC substrate (TanKeBlue Semiconductor Co. Ltd., Beijing, China) was cleaned using a two-step procedure. To remove organic contamination, the substrates were cleaned sequentially twice with trichloroethylene, acetone, methanol, and deionized water. Second, to remove the native oxide layer on the surface, the 6H-SiC substrate was immersed for 30 s in a dilute hydrofluoric acid (HF 50%) solution (H_2O:HF = 10:1) three times. Then, approximately 60 nm of Ni was deposited on the 6H-SiC substrate using direct current (DC) magnetron sputtering at 50 W for 15 min after pre-sputtering for about 15 min. To prepare thin samples for TEM, two Ni/SiC samples were attached to each other using G-1 epoxy (Gatan Inc., Pleasanton, CA, USA) and cut to dimensions of 1 × 1.5 mm using a diamond saw. The sample was then mechanically thinned to less than 0.5 μm by wedge-type polishing with a tripod polisher. The wedge sample was attached to a Mo TEM aperture grid with 1.5 mm hole. Using Ar^+ ion milling (PIPS, Gatan Inc.), the sample was further thinned under the following conditions: accelerating voltage of 4.5 kV, milling angle of 4° for both top/bottom guns, and single sector beam modulation mode.

In situ heating experiments were carried out via TEM (JEM-3010, JEOL Ltd., Akishima, Tokyo, Japan) operated at 300 keV by using a double-tilt heating holder (EM-31050, JEOL Ltd.) and a heater control unit (EM-SHU2, JEOL Ltd.). Since the heating system uses an R-type thermocouple, the measured and actual temperature of the TEM sample may be slightly different. Therefore, the heating holder was calibrated according to a procedure described elsewhere [11]. In this study, the temperature was increased to 550 °C after stabilizing the sample at 500 °C for a few minutes to observe the initial reaction. The microstructural evolution during heating was recorded using a charge-coupled device (CCD) camera (ORIUS SC1000, Gatan Inc., Pleasanton, CA, USA). After the in situ experiment, the microstructure of Ni silicide phases and the elemental distribution were analyzed in detail using spherical-aberration-corrected TEM (JEM-ARM 200F, JEOL Ltd.).

3. Results and Discussion

The current study focuses on the mechanism of the interfacial reaction and the behavior of carbon during in situ heating under TEM observation. Fig. 1(a) shows a sequence of TEM images captured from the video (see Supporting Information) recorded during the in situ heating of Ni/6H-SiC specimen at 550 °C for approximately 30 min. The as-deposited Ni/6H-SiC specimen is shown in the first image. As the temperature increased to 500 °C (second image), the reaction started slowly. When the temperature reached 550 °C, the reaction proceeded continuously, and Ni silicide formed due to the diffusion of Ni atoms into the SiC substrate. While the temperature was maintained for 30 min, the Ni silicide layer grew thicker at the expense of the SiC substrate. After heating, as shown in the last image of Fig. 1(a), approximately 50 nm and 15 nm thick Ni silicide layers were formed below and above the initial Ni/6H-SiC interface (marked with a yellow dashed line), respectively. This suggested that the diffusion rate of Ni is faster than that of Si.

To identify the phases formed during the in situ heating experiment, an electron diffraction analysis was carried out. As shown in Fig. 1(b), a nano-beam electron diffraction (NBED) pattern was obtained for the upper and the lower area of Ni silicide. The upper Ni silicide phase that formed above the initial interface was confirmed to be $Ni_{31}Si_{12}$ with the [3–34] zone axis NBED pattern. A fast Fourier transform (FFT) pattern

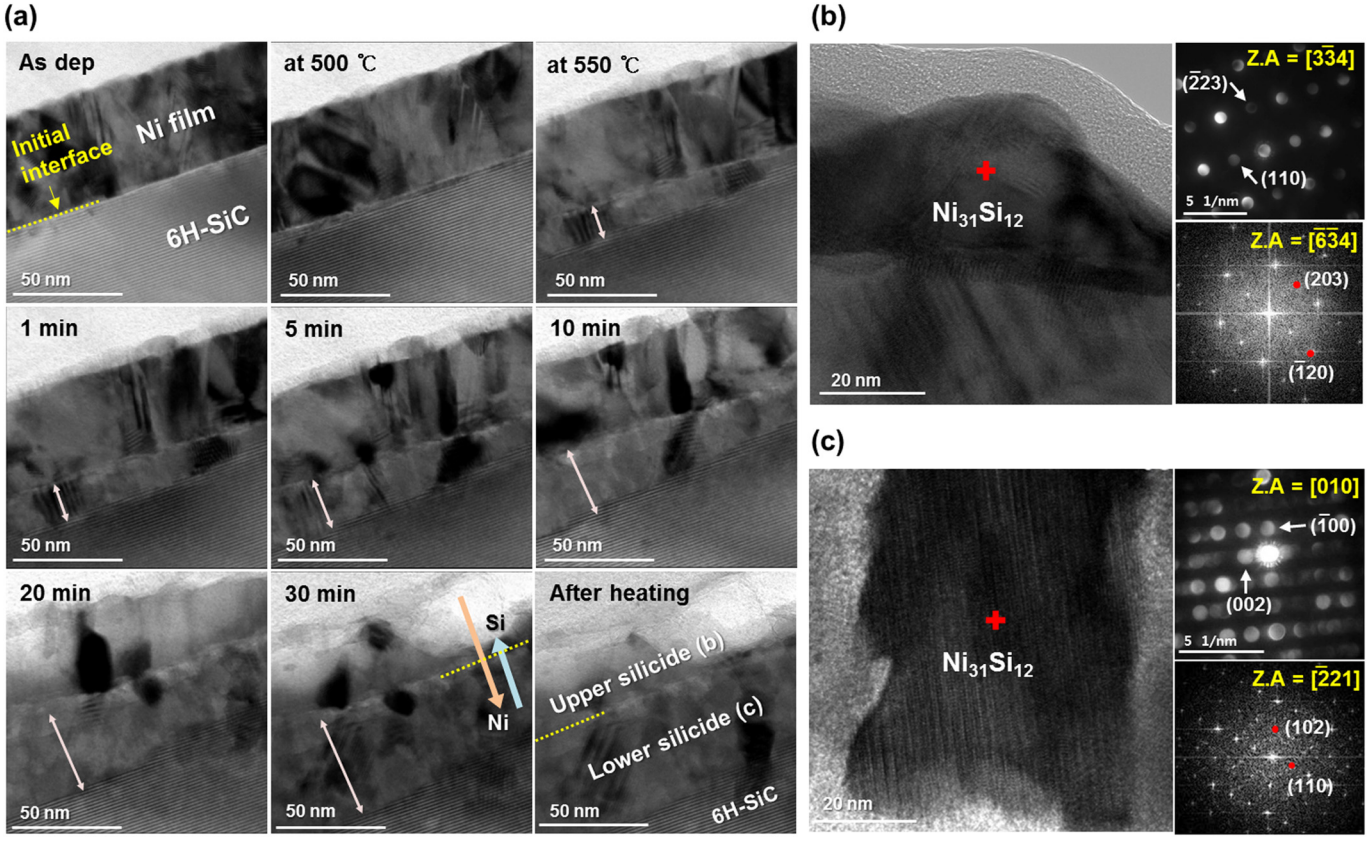

Fig. 1. (a) In situ TEM images captured from the video before heating (top left) and after annealing at 550 °C for 1 min, 5 min, 10 min, 20 min, and 30 min. After heating, NBED and FFT patterns were obtained to characterize the phases in the (b) upper and (c) lower area of Ni silicide. Both are the $Ni_{31}Si_{12}$ phase. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)