

A method of Ga removal from a specimen fabricated on MEMS-based chip for in-situ transmission electron microscopy

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Abstract

In-situ transmission electron microscopy (TEM) holders, which are widely used in recent years, employ a chip-type specimen stage. To prepare the specimen on the microelectromechanical system (MEMS)-based chip, focused ion beam (FIB) and ex-situ lift-out (EXLO) techniques has been widely used. However, thin foil specimens prepared using the FIB inevitably contain the contamination induced by Ga^+ ions. In particular, when the specimen is heated for real time observation, it is observed that Ga^+ ions influence the reaction or aggregate in the protection layer. An effective method of removing the Ga residue is demonstrated using Ar^+ ion milling within FIB. In the case of lifting the thin foil specimen from the trench by the EXLO technique, Ga still remained even if Ar^+ ion milling was conducted. To avoid this problem, the thin foil specimen was attached to FIB lift-out grid, performing Ar^+ ion milling, and then transferred to a MEMS chip using EXLO technique. The removal of the Ga residue was confirmed using energy dispersive spectroscopy (EDS).

1. Introduction

Research on in-situ transmission electron microscopy (TEM), an analytical technique that allows real-time observation of microstructural evolution induced by external stimulations such as heating, electrical biasing, and mechanical deformation, is actively being conducted. In recent years, as the use of microelectromechanical systems (MEMS)-based chips for in situ TEM experiments increases, the preparation of specimens becomes even more challenging. One of the most widely used methods is to fabricate thin lamellae via focused ion beam (FIB) (Duchamp et al., 2014; Mele et al. 2016; Vijayan et al. 2017). This method has the advantage of being able to fabricate a specimen with a uniform thickness and the entire specimen preparation is completed only within the FIB. However, the supporting film in the chip may be torn or the surface of specimen may be damaged during FIB milling. Also, lift-out for positioning the lamella on MEMS chips performed inside the FIB (e.g., in-situ lift-out (INLO)) requires multiple and complex manipulation and an special inclined stage that minimizes the ion flux experienced by the chip during FIB milling (Duchamp et al., 2014; Vijayan et al. 2017; Pivak et al. 2018).

Alternately, the MEMS chip specimen can be prepared using the ex-situ lift-out (EXLO) method with FIB to overcome the abovementioned limitations. The EXLO method is the first lift-out technique to be implemented for FIB-prepared specimens and has been applied to various material systems (Herlinger et al., 1996; Giannuzzi et al., 1997). The EXLO method is a fast and simple technique to manipulate a specimen for analysis in less than 5 min per specimen (Giannuzzi et al., 2015). Also, this method is suitable for precise positioning of FIB-prepared specimens during transfer onto the MEMS chips. However, there is still an major drawback that residual Ga accumulated during FIB milling remains in the specimen. A lot of studies have been conducted to remove the residual Ga. Usually, the final thinning has been conducted with the a low energy (less than 3 keV) within the FIB. In addition, as a method of removing Ga^+ ions from the external of the FIB, research was conducted using a equipment such as plasma cleaner applying a bias (Ko et al., 2007), NanoMill (Fischione, USA) (Unocic et al., 2010) and PicoMill (Fischione,

USA) (Campin et al., 2019). However, these methods are difficult to apply to FIB-prepared thin specimens in a trench to use the EXLO technique. In addition, it is difficult to simultaneously remove Ga⁺ ions from both sides of a specimen transferred onto a MEMS chip. Therefore, in this study, we compared the thin foil specimens fabricated using the FIB/EXLO methods were compared with specimens fabricated with conventional mechanical polishing/ion milling and graphene encapsulation to observe the problems caused by Ga⁺ ions, and proposed a method to remove Ga⁺ ions by performing Ar⁺ ion milling within the FIB.

2. Materials And Methods

Deposition

Si (100) wafers were cleaned three times with ethanol and acetone to remove organic contaminants from the surface. After that, the Si wafers were immersed in a dilute hydrofluoric acid (HF 50%) solution (H₂O:HF = 10:1) to remove the native oxide layer. Then, 30 nm-Ni and 30 nm-TaN were sequentially deposited on one Si wafer, and 30 nm-Er and 30 nm-TaN was sequentially deposited on the other Si wafer by DC magnetron sputtering.

Fabrication of thin foil specimen via mechanical polishing and ion milling

To prepare thin foil TEM specimens via mechanical polishing and ion milling, the metal deposited Si wafer was cut in half and the metal-deposited sides were bonded to each other using G-1 epoxy (Gatan Inc., Pleasanton, CA, USA). And this sandwich wafer was cut into small pieces (1 · 1.5 mm) using a low speed diamond saw for further thinning. The cut specimens were mechanically thinned using SiC paper, diamond suspensions (6 μm, 3 μm, and 1 μm,) and colloidal silica (0.05 μm) sequentially. The flat polished specimen was attached to a Mo TEM aperture grid with 1.5 mm hole. Using Ar⁺ ion milling (PIPS, Gatan Inc.), the specimen was further thinned under the following conditions: accelerating voltage of 4 kV, milling angle of 2°~ 4° for both top/bottom guns, and dual beam modulation mode.

Fabrication of thin foil specimen on MEMS-based chip via FIB and EXLO technique

Experiments were conducted using a Hitachi NX2000 triple-beam FIB system (Hitachi Ltd., Japan). First, electron beam induced deposition (EBID) and ion beam induced deposition (IBID) are sequentially performed on the metal deposited Si specimen to produce a protection layer in the FIB. After that, a large beam current was used to create a large trench and the specimen was milled using successively smaller beam currents as the region of interest was approached. And Ar⁺ ion milling was conducted in two different ways to remove Ga residue as shown in Fig. 1. First, the region of interest in the trench was milled into thin foil specimen less than 100 nm-thick as suggested in the conventional EXLO technique. Then, Ar⁺ ion milling was performed in that state and the thin foil specimen was lifted and transferred onto the MEMS-based chip using the EXLO technique (Fig. 1a). The second method is the proposed modified method, attaching the specimen to the grid, Ar⁺ ion milling and transferring onto the MEMS-

based chip using the EXLO technique as shown in the Fig. 1b. The specimen was milled to a thickness of $\sim 1 \mu\text{m}$ in a trench and attached to the FIB lift-out TEM grid (NANOMESH, Hitachi Ltd., Japan) using carbon-IBID at 30 keV and 80 pA with 0.1 s dwell time. Next, the region of interest was further etched using a high-energy Ga^+ ion beam at 30 keV and 1.5 nA, and subsequently thinned using a low-energy Ga^+ ion beam at between 5 and 10 keV and 40 pA to obtain a thickness below 80 nm. Finally, Ar^+ ion milling was performed at 1 keV and 19 nA for four direction rotated about 15° from the home position; front side, back side, front side turned 180° , and back side turned 180° . Milling for 2 \sim 4 min in each direction, and the last milling was done on the front side or back side turned 180° direction to prevent re-deposition by grid. After that, EXLO equipment was used to detached the specimen from the grid and transfer it to the desired area on the MEMS based chip.

Fabrication of graphene encapsulated thin foil specimen

Graphene encapsulated specimens are fabricated by applying the mechanical exfoliation method. The first step of the process included preparation of a 300 nm SiO_2/Si and a polymethylmethacrylate (PMMA)/lift-off resist (LOR)/ SiO_2/Si wafer and then graphene separated from highly oriented pyrolytic graphite (HOPG) transferred on both wafers. A FIB-prepared specimen was transferred onto the prepared graphene/ SiO_2/Si wafer using an EXLO technique. Afterward, the LOR layer was removed using a KOH solution from the graphene/PMMA/LOR/ SiO_2/Si wafer and subsequently covered on the specimen/graphene/ SiO_2/Si wafer.

Characterization

The microstructure and elemental composition of the TEM specimens were evaluated using TEM (JEM-ARM 200F, JEOL Ltd.) equipped with energy dispersive X-ray spectroscopy (EDS; INCA Energy TEM, Oxford Instruments) and electron energy loss spectroscopy (EELS; 965 GIF Quantum ER, Gatan Ltd.). Fusion Thermal E-chips (E-FHDC, Protochips Inc.) and a Fusion 500™ TEM holder (Protochips Inc.) were used for in situ heating experiments.

3. Results And Discussion

First, the silicide reactions after heat treatment of Si-based binary thin foil specimens fabricated by two different methods were compared. Figure 2a is a TaN/Ni/Si thin foil specimen prepared via mechanical polishing and ion milling, showing the 50 nm-thick Ni-silicide reaction layer. Meanwhile, Fig. 2b shows a TaN/Ni/Si thin foil specimen fabricated using the FIB and EXLO technique, and the length of the reaction layer after heat treatment was about 114 nm. The difference in reaction between the two specimens was also observed in the EDS line profile results. In the former specimen, only Ni and Si were detected in the reaction layer, whereas in the latter specimen, $\sim 10 \text{ at}\%$ Ga was detected in the reaction layer as well as the elements that participated in the reaction. As a result, we observed that Ga residue was left on the thin foil specimen owing to FIB milling, and affected the silicide reaction even though the specimen was heat-treated under the same condition. Another phenomenon induced by Ga^+ ions was observed in Fig. 2c.

This Si-based binary system (TaN/Er/Si thin foil specimen) was also fabricated in the same way as the specimen of Fig. 2b, and Ga⁺ ions agglomerated in the form of cluster on the protection layer of the specimen after heat treatment. Therefore, removal of Ga residue is essential, and Ar⁺ ion milling method in FIB was used in this study.

In order to more reliably confirm the effect of Ga⁺ ion removal by Ar⁺ ion milling, the thin foil specimen was completely encapsulated using graphene. Because the graphene has no material permeability, except for hydrogen gas, Ga⁺ ions contained in the specimen cannot escape to the outside or enter from the outside. Figure 3 shows the result of Ar⁺ ion milling on the thin foil specimen located inside the trench. As a result of heating of the graphene-encapsulated TaN/Ni/Si thin film specimen as shown in Fig. 3a, about 8.3 at% Ga was detected along the Ni-silicide reaction layer as previously observed. In addition, Ga was also detected in a region where Ni diffused onto the Si substrate through EDS mapping. In the TaN/Er/Si thin foil specimen (Fig. 3b), Ga was mainly distributed in the protection layer deposited during FIB after heat treatment. The reason that Si is also detected in the protection layer can be attributed to the use of Fusion Thermal E-chip employing SiC substrate. Unlike the circular shape (actually, sphere shape in 3-D) observed in Fig. 2c, Ga formed irregular shapes in graphene encapsulated specimen. Ga shows the viscous behavior of the liquid owing to its a very low melting point of 29.8 °C and low surface free energy (Stevie et al., 2005). Therefore, Ga can move together during the diffusion of reacting substances by the capillary force of graphene or creates irregular shapes under pressure by negative volume expansion. As a result, for specimens with deep trench, Ar⁺ ion milling is not effective in removing Ga⁺ ions and most of them remain, affecting the reaction. This may be due to the fact that the specimen is re-deposited with Ga⁺ ions or other materials. Since Ar⁺ ion beam is not a focused beam, considerably large area of specimen is milled by the Ar⁺ ions. Therefore, the same problem will always occur even if the specimen stage is rotated or tilted as long as the the region of interest is located inside the trench. This phenomenon reduces the reliability of TEM analysis.

To overcome abovementioned limitation, the specimen was fabricated using the method of attaching to the FIB lift-out grid. It should be noted that the specimen is attached to the grid under specific conditions unlike the conventional FIB lift-out method, as described in the Materials and Methods section. This is because, the thin foil specimen must be fixed to the grid for further milling and Ar⁺ ion milling, but easily detached from the grid when transferring to MEMS-based chip using the EXLO technique. As a result, in the TaN/Ni/Si specimen as shown in the Fig. 4a, Ga was not detected in the reaction layer by EDS analysis. In addition, the reaction layer formed was also observed to be similar to Fig. 1a. In the TaN/Er/Si specimen of Fig. 4b, the amount of Ga observed in the protection layer was significantly reduced. Although Ga was present at the thick part of the specimen, the overall result was not affected. Therefore, it can be concluded that the method proposed in this study was able to effectively remove Ga⁺ ions. This method is simple and easy, and has the advantage that all milling process of the specimen can be completed within the FIB, and Ga ions can be removed from both sides of the specimen.

4. Conclusion

For a specimen on the MEMS-based chip prepared by the conventional FIB and EXLO method, the artifacts induced by Ga⁺ ions were observed; Ga⁺ ions influenced the binary system reaction and agglomerated in the protection layer. In other words, in the case of thin foil specimen in the trench, even if the specimen was prepared by the conventional EXLO method of lifting after Ar⁺ ion milling, Ga still remained and affected the reaction during the in-situ experiment. To overcome this problem, we propose a modified method of attaching a thin foil specimen to the FIB lift-out grid by ion beam induced carbon deposition, performing Ar⁺ ion milling, and then transferring it to a MEMS chip using EXLO method. As a result, it was observed that most of the Ga residue contained in the specimen were removed.

5. List Of Abbreviations

TEM: Transmission electron microscopy, FIB: Focused ion beam, EXLO: ex situ lift-out, EDS: Energy dispersive X-ray spectroscopy, HAADF: High-angle annular dark-field, MEMS: Microelectromechanical, STEM: Scanning transmission electron microscopy

6. Declarations

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Authors' contributions

YK have contributed to producing experimental resources, data acquisition and TEM analysis and to writing the manuscript. BSA have contributed to sample preparation and data analysis. YJS have contributed to performing FIB experiment. CWY has supervised the project along with advising and reviewing the manuscript. The authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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Figures

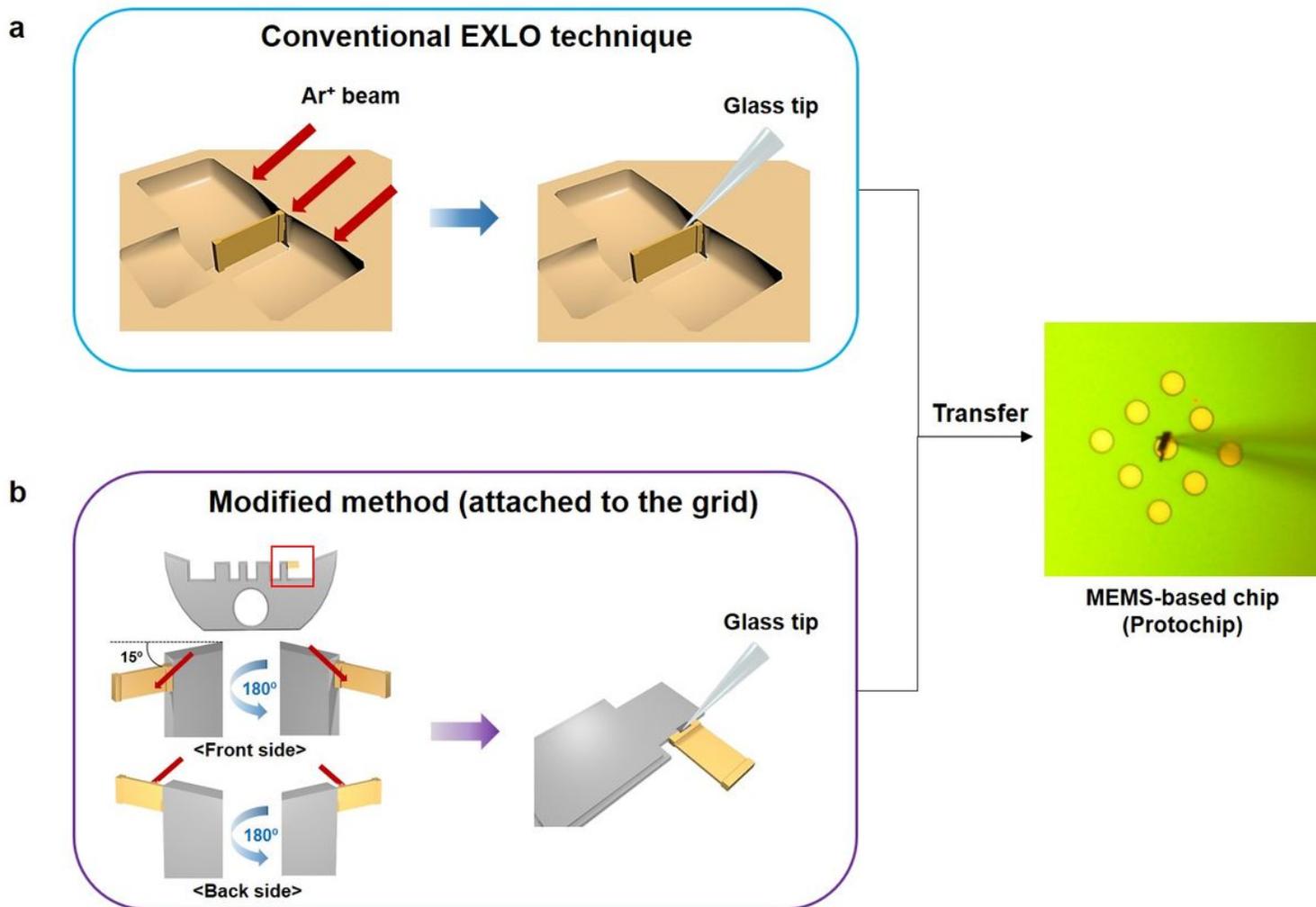


Figure 1

Schematic diagram of two different Ar^+ ion milling methods to remove Ga^+ ions.

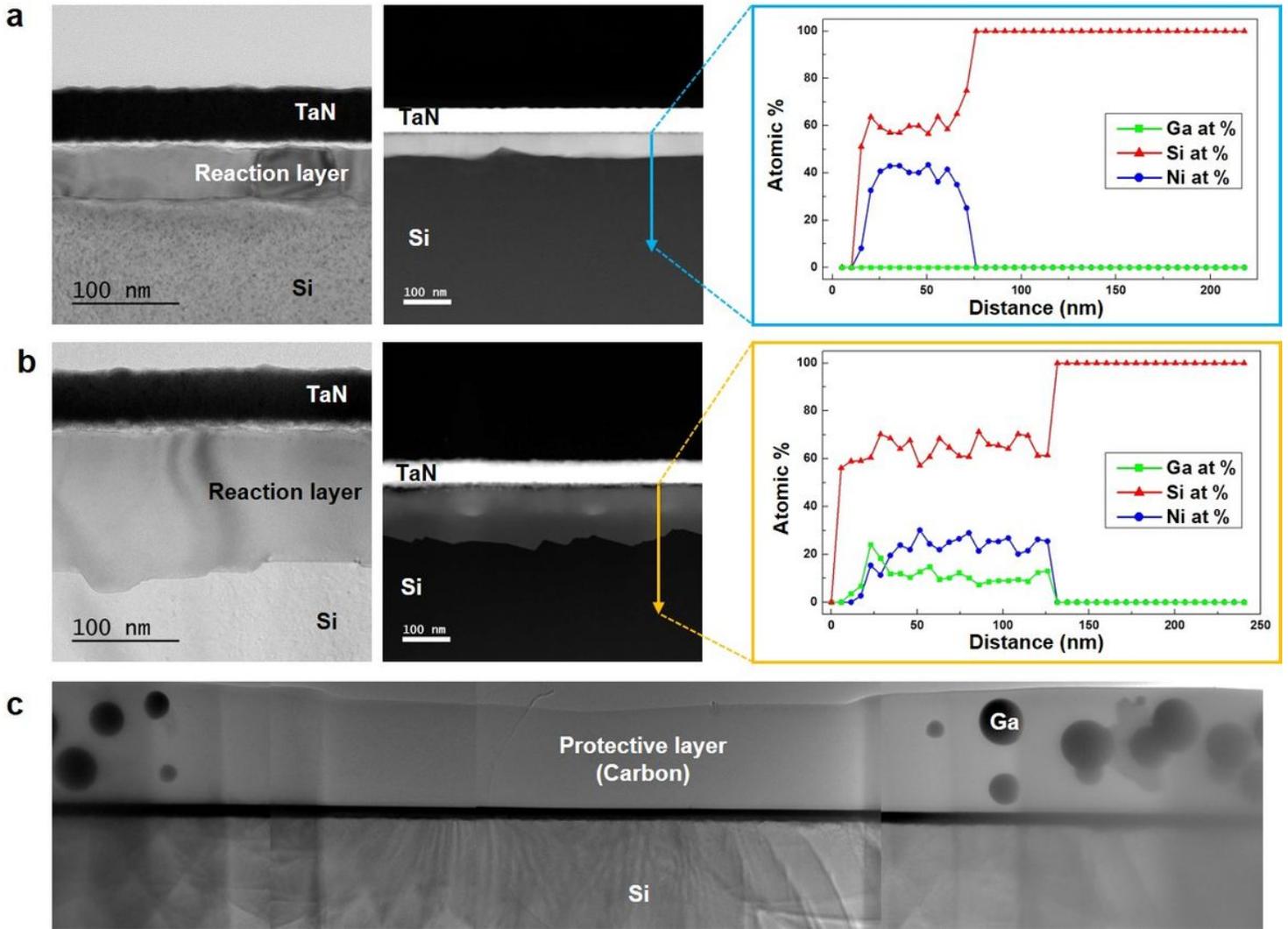


Figure 2

The TEM/high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) images and EDS line profile of heat-treated TaN/Ni/Si thin foil specimen prepared via a) mechanical polishing and ion milling, and b) FIB and EXLO technique c) The low magnification TEM image of TaN/Er/Si thin film specimen prepared via FIB and EXLO technique

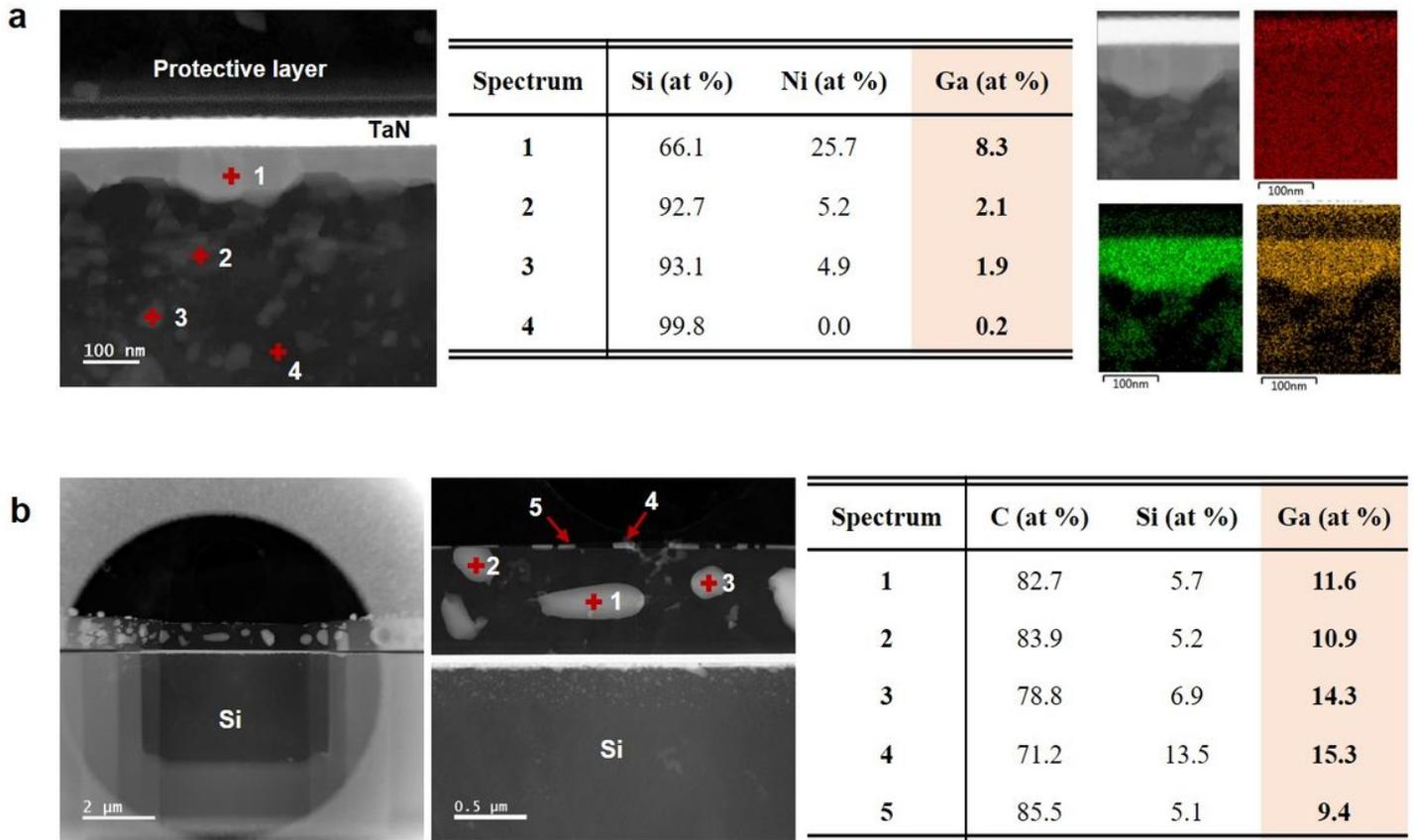


Figure 3

Results after Ar⁺ ion milling of the specimen in the trench a) The HAADF-STEM image and the result of EDS analysis of heat-treated graphene encapsulated TaN/Ni/Si thin foil specimen. Si K series EDS mapping is shown in red, Ni K series EDS mapping is shown in green, and Ga L series EDS mapping is shown in orange. b) The HAADF-STEM image and chemical composition of heat-treated graphene encapsulated TaN/Er/Si thin film specimen

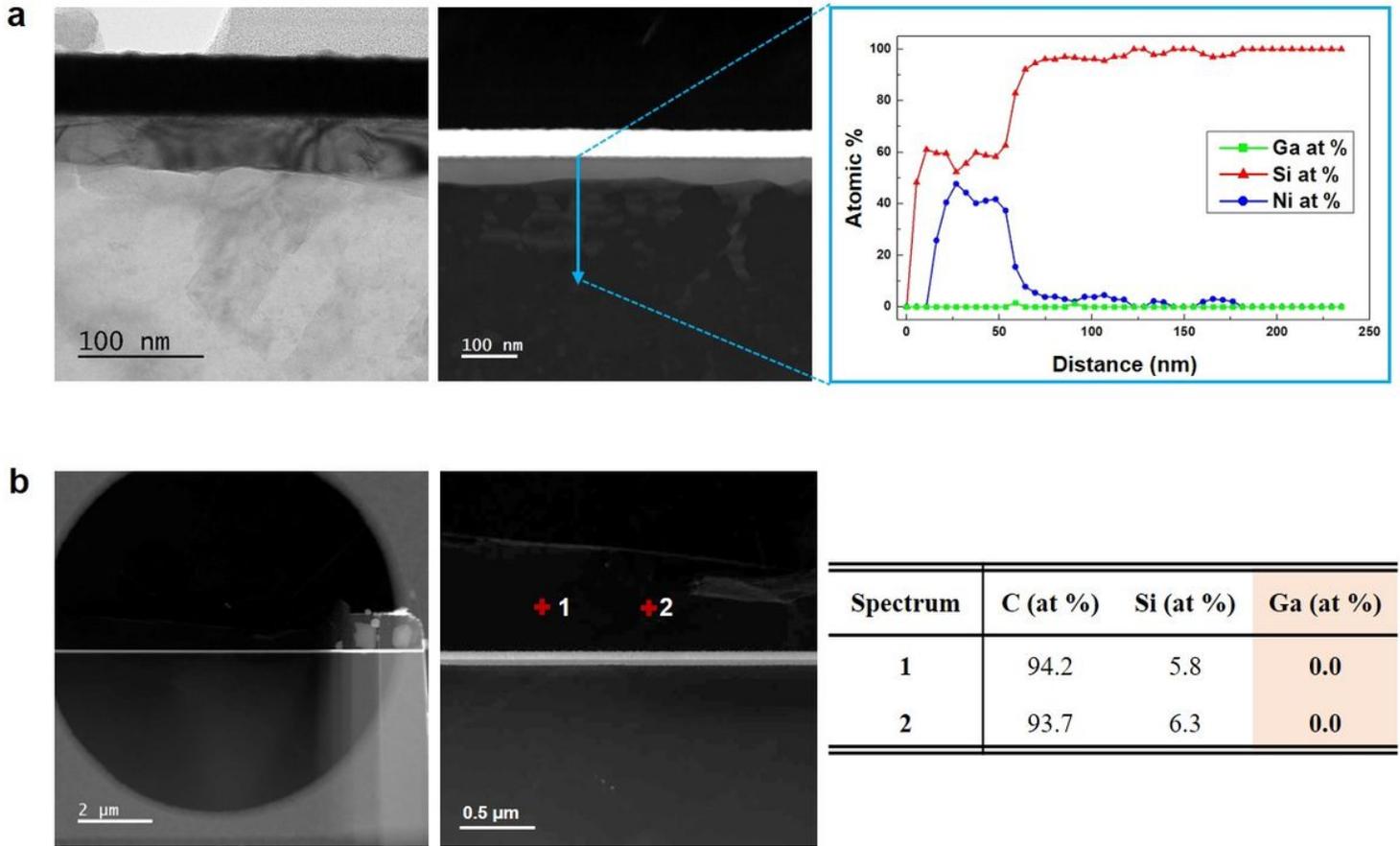


Figure 4

The result after Ar⁺ ion milling the specimen attached to the FIB lift-out grid a) The TEM/HAADF-STEM images and EDS line profile of heat-treated graphene encapsulated TaN/Ni/Si thin foil specimen b) The TEM/HAADF-STEM images and chemical composition of heat-treated graphene encapsulated TaN/Er/Si thin foil specimen