

In Situ Transmission Electron Microscopy Study on the Reaction Kinetics of the Ni/Zr-interlayer/Ge System

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The reaction kinetics of the growth of Ni germanide in the Ni/Zr-interlayer/Ge system was investigated using isothermal in situ annealing at three different temperatures in a transmission electron microscope. The growth rate of Ni germanide in the Ni/Zr-interlayer/Ge system was determined to be diffusion controlled and depended on the square root of the time, with the activation energy of 1.04 ± 0.04 eV. For the Ni/Zr-interlayer/Ge system, no intermediate or intermixing layer between the Zr-interlayer and Ge substrate was formed, and thus the Ni germanide was formed and grew uniformly due to Ni diffusion through the diffusion path created in the amorphous Zr-interlayer during the annealing process in the absence of any intermetallic compounds. The reaction kinetics in the Ni/Zr-interlayer/Ge system was affected only by the Zr-interlayer.

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INTRODUCTION

Germanium (Ge) is one of the first materials to receive wide attention for use in semiconductor device fabrication, and Ge metal oxide semiconductor field effect transistors (MOSFETs) are considered to be promising devices for future high-speed complementary metal-oxide-semiconductor technology due to their high carrier mobility. It is well known that self-aligned germanide (salmanide), like self-aligned silicide (salicide), is effective in reducing the parasitic source/drain resistance. Germanide can be formed by a solid-state reaction between a metal and Ge. Among the various metal germanides, Ni germanide is being considered as the most promising salmanide material for Ge MOSFET technology due to its low formation temperature, only a nickel mono-germanide phase and low sheet resistivity (Balakrishnan et al., 2005; Hsu et al.,

2005; Zhang et al., 2005; Zhu & Nakajima, 2005). However, one challenge of Ni germanide is its low thermal stability due to agglomeration and/or penetration of Ni germanide itself (Zhang et al., 2008). There have been many attempts to improve the thermal stability of Ni germanide by addition of alloying element or interlayer. In our previous studies (Lee et al., 2007, 2008, 2013), the formation and microstructural evolution of the Ni germanides formed in Ni/metal-interlayer/Ge systems, i.e., Ni/Ta-interlayer/Ge and Ni/Zr-interlayer/Ge systems, were examined as a function of annealing temperature in ex situ and in situ annealing experiments. It was found that the sheet resistance values of the germanides formed in the Ni/metal-interlayer/Ge systems remained stable at lower values than those in the Ni/Ge system at high temperatures. An improvement in the thermal stability of the Ni germanide was caused by a reduction in the surface

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free energy due to the metal-rich layer formed on top of the newly formed Ni germanide film. However, in order to fully understand the effects of interfacial phenomena on the thin film reaction, it is important to find the kinetic parameters for the growth of Ni germanide and the thermodynamic information about these systems. One of the many advantages of in situ transmission electron microscopy (TEM) is that the kinetic parameters can be obtained simultaneously with a direct observation of the reactions.

In this study, the reaction kinetics of the growth of Ni germanide in the Ni/Zr-interlayer/Ge system was examined. In order to obtain the kinetic parameters of the systems, isothermal in situ annealing experiments were carried out in a TEM equipped with a specimen-heating holder. The variation in the thickness of the Ni germanide layer during annealing at different temperatures as a function of annealing time was measured using the TEM micrographs.

MATERIALS AND METHODS

A *p*-type (1 0 0) Ge wafer was cleaned sequentially with trichloroethylene, acetone, methanol, deionized water, and a dilute hydrofluoric acid (HF) solution (HF:H₂O=1:100), and was immediately loaded into a DC magnetron sputtering system. Then approximately 1 nm-thick Zr and 15 nm-thick Ni films were deposited sequentially at room temperature under Ar gas pressure of 0.5 Pa after reaching a base pressure below 2.0×10^{-5} Pa. Cross-sectional high resolution (HR)-TEM micrograph of the as-deposited specimen of the Ni/Zr-interlayer/Ge system formed by this way is shown in Fig. 1. For TEM analysis, conventional ion-milled specimens were

prepared by mechanical grinding using a tripod polisher (model 590; South Bay Technology Inc., USA) followed by Ar-ion milling in a precision ion polishing system (PIPS; Gatan Inc., USA). In particular, the TEM specimens were fixed on Mo oval grids that can provide the high thermal stability required for the in situ annealing experiments.

One of the important experimental parameters in the in situ annealing experiment in a TEM is the temperature of a specimen which is conventionally measured by thermocouple. As the thermocouple of the specimen-heating holder is not in direct contact with the specimen, the measured temperature may be different from the temperature of the area of interest in the TEM specimen. Therefore, in order to observe the reaction of the specimen according to temperature, it is important to measure the actual temperature of the specimen during an in situ heating experiment. This can be achieved by the calibration experiment with pure element specimens. In this study, the calibration curves were obtained using pure Sn and pure Al. The detailed procedure of the calibration experiment is described in elsewhere (Lee et al., 2015).

The other important experimental parameter is a dimension such as thickness of the thin film layers, length and width of nanostructures, etc. It can be determined easily and accurately using digital TEM images. In order to measure the thickness of a thin film, it is essential to calibrate the size of the digital image at each magnification. Therefore, we perform this calibration at each magnification for the UltraScan CCD camera (USC 1000; Gatan Inc.) attached to the TEM (JEM-3011; JEOL Ltd., Japan) using the MAG**I**CAL® calibration reference standard (SPI Supplies, USA).

RESULTS AND DISCUSSION

In order to study the kinetic behavior of the Ni-Ge reaction in the Ni/Zr-interlayer/Ge system, isothermal annealing studies were conducted in a TEM equipped with a specimen-heating holder (EM-31050; JEOL Ltd.) at different temperatures. Isothermal in situ annealing experiments were carried out at 160°C, 180°C, and 200°C. Fig. 1 shows a cross-sectional HR-TEM micrograph of a Ni film and a Zr-interlayer deposited on a Ge substrate observed at room temperature. The measured thicknesses of the Ni film and Zr-interlayer were approximately 153 Å and 10 Å, respectively.

The microstructural evolution of the interface between the Zr-interlayer and the Ge substrate is displayed in a series of cross-sectional HR-TEM micrographs in Fig. 2 which was recorded using an UltraScan CCD camera during isothermal in situ annealing at 160°C. The Ni germanide layer formed underneath the Zr-interlayer and grew to about 17 Å in thickness when the temperature was raised from room temperature up to 160°C at the ramp rate of 16°C/min, and the TEM specimen was stabilized for recording the images. As

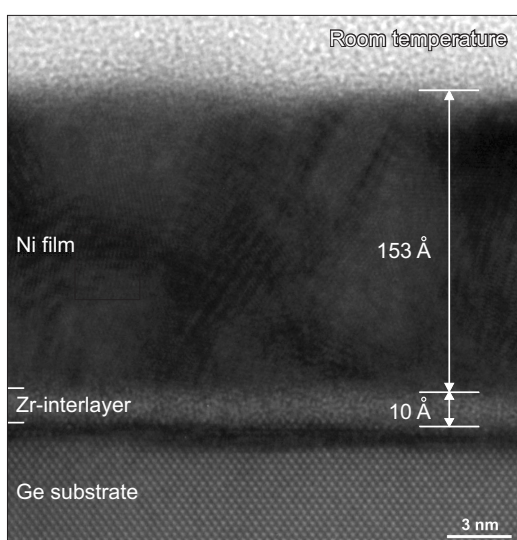


Fig. 1. Cross-sectional high resolution transmission electron microscopy micrograph of Ni film and Zr-interlayer deposited on Ge substrate observed at room temperature.

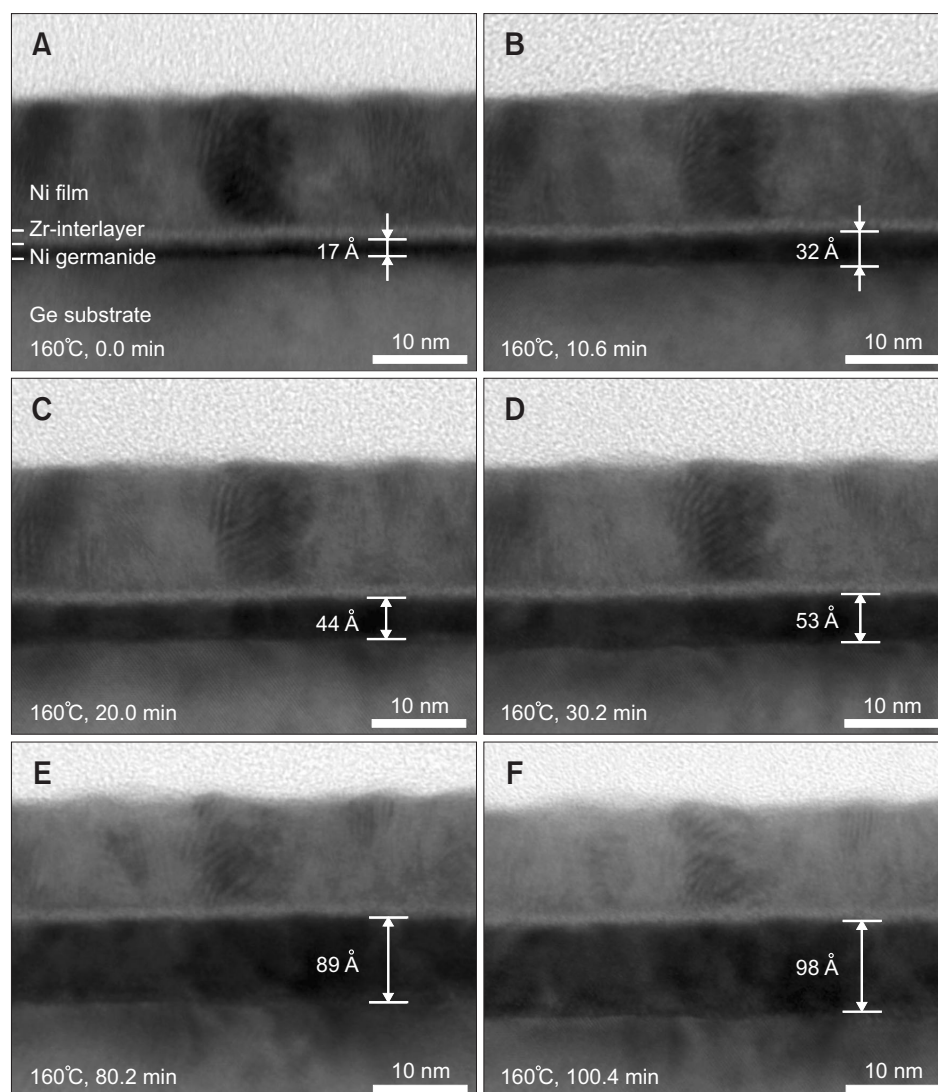


Fig. 2. (A-F) A series of cross-sectional transmission electron microscopy micrographs of Ni/Zr-interlayer/Ge system, which was recorded by UltraScan CCD camera (Gatan Inc.) during the isothermal in situ annealing at 160°C as a function of annealing time.

the in situ annealing time increased, the Ni germanide layer grew thicker relatively uniformly, as shown in Fig. 2B-F. The thicknesses of the Ni germanide layer were measured to be 32 Å, 44 Å, 53 Å, 89 Å, and 98 Å for annealing time of 10.6 min, 20.2 min, 30.2 min, 80.2 min, and 100.4 min, respectively. The Ni germanide thickness as a function of the in situ annealing time was measured by taking the average of the thickness measured at 5 different locations. There was no noticeable change in the thickness of the Zr-interlayer on top of the Ni germanide.

Similarly, isothermal in situ annealing experiments were also carried out at 180°C and 200°C. Fig. 3 and 4 show the microstructural evolution of the interface between the Zr-interlayer and the Ge substrate during isothermal in situ annealing at 180°C and 200°C, respectively. Due to a limitation of ramp rate, the Ni germanide formed and grew until the temperature reached at the target temperature of isothermal

in situ annealing experiment. Thus, the initial thickness of the Ni germanide at the starting point of the isothermal in situ annealing experiment increased as annealing temperature increased, for instance, 17 Å for 160°C, 49 Å for 180°C, and 94 Å for 200°C. As shown in Fig. 3, for the isothermal in situ annealing experiment at 180°C, the thicknesses of the Ni germanide layer were measured to be 49 Å, 99 Å, 131 Å, 154 Å, 176 Å, and 194 Å for the annealing time of 0.0 min, 20.1 min, 40.2 min, 60.2 min, 80.1 min, and 99.8 min, respectively. In the case of the isothermal in situ annealing experiment at 200°C, as shown in Fig. 4, the thicknesses of the Ni germanide layer were measured to be 94 Å, 118 Å, 129 Å, 166 Å, 196 Å, and 220 Å for the annealing time of 0.0 min, 5.0 min, 9.9 min, 19.8 min, 29.8 min, and 40.1 min, respectively.

It was observed that an intermediate or intermixing layer was not formed in the interface between the Zr-interlayer and the Ge substrate, and that the newly formed Ni germanide

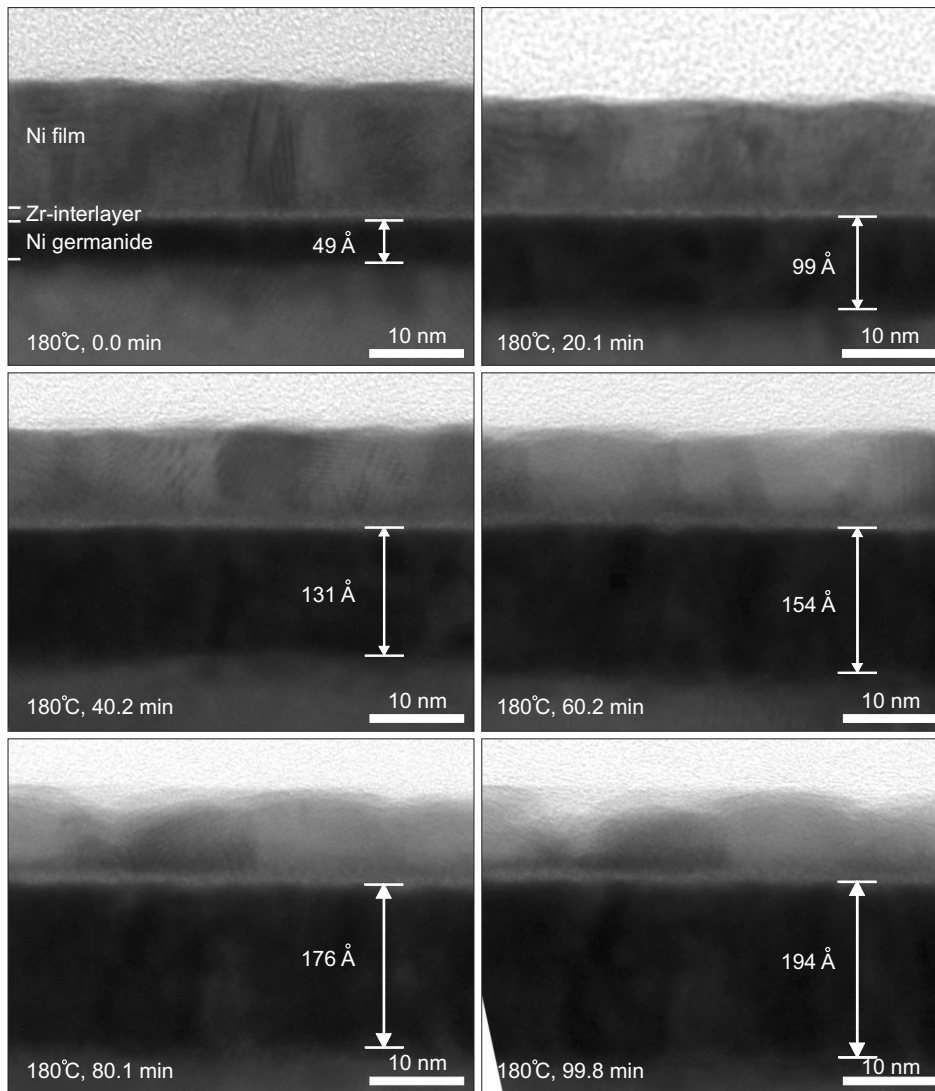


Fig. 3. A series of cross-sectional transmission electron microscopy micrographs of Ni/Zr-interlayer/Ge system, which was recorded by UltraScan CCD camera (Gatan Inc.) during the isothermal in situ annealing at 180°C as a function of annealing time.

layers that grew during in situ annealing at these temperatures were more uniform compared with those in Ni/Ge and Ni/Ta-interlayer/Ge systems in our previous study (Lee et al., 2015). In the case of the Ni/Ta-interlayer/Ge system where the Ta-interlayer is applied instead of the Zr-interlayer in order to improve the thermal stability of the Ni germanide layer, in contrast, it was reported that the amorphous Ni-Ta-Ge ternary layer was formed between the Ta-interlayer and the Ge substrate, and then, the ternary amorphous layer became thinner and the Ni germanide layer grew thicker with increasing annealing time.

The thickness of the Ni germanide layer as determined from the isothermal in situ annealing experiments is plotted in Fig. 5 as a function of the annealing time. It shows the kinetic data for the growth of Ni germanide in the Ni/Zr-interlayer/Ge system with annealing time during isothermal in situ annealing at 160°C, 180°C, and 200°C. Since a diffusion-

controlled reaction is typically observed in this system, the activation energy can be calculated from the isothermal in situ annealing data at three different temperatures.

For the diffusion-controlled reaction (Cotts et al., 1986; DeAvillez et al., 1990),

$$X \frac{dx}{dt} = K \quad (1)$$

where X is the thickness of the Ni germanide layer and K is the parabolic reaction rate constant. By integrating this equation from X_i , the initial thickness of the Ni germanide layer, to X_p , the thickness of the Ni germanide layer after annealing at a temperature T for time t , we obtain the following equation:

$$\frac{X_p^2 - X_i^2}{2t} = K \quad (2)$$

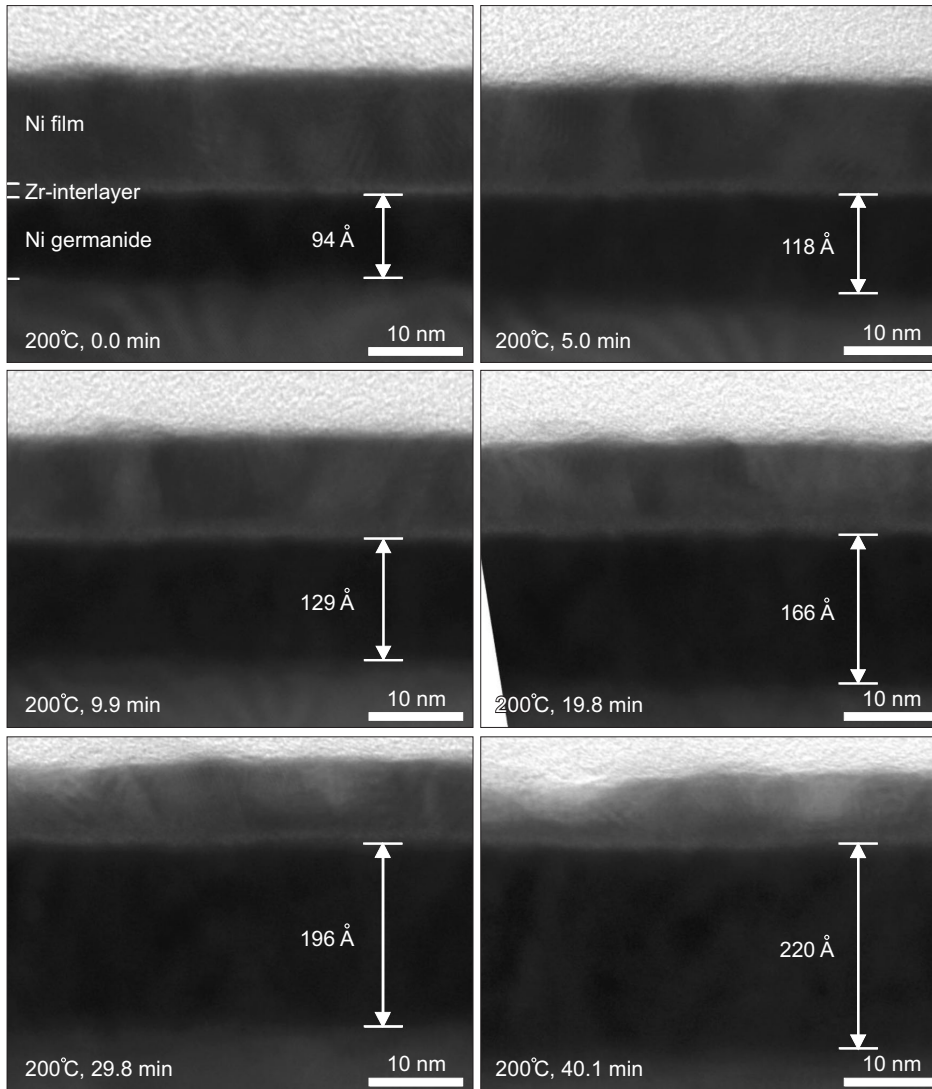


Fig. 4. A series of cross-sectional transmission electron microscopy micrographs of Ni/Zr-interlayer/Ge system, which was recorded by UltraScan CCD camera (Gatan Inc.) during the isothermal in situ annealing at 200°C as a function of annealing time.

Using the data obtained at three different temperatures, the values for K were calculated. The growth of the Ni germanide in the Ni/Zr-interlayer/Ge system adheres to a parabolic rate law, as shown in Fig. 5. The activation energy barrier can be derived by using the following Arrhenius equation:

$$K = A \exp \left[-\frac{E_a}{RT} \right] \quad 3)$$

Fig. 6 shows an Arrhenius plot of the natural log of the parabolic reaction rate constant, $(X_i^2 - X_i^2/2t)$ versus $1/\text{absolute temperature}$ using the data in Fig. 5. From the slope of this plot the activation energy for the growth of the Ni germanide layer in the Ni/Zr-interlayer/Ge system was found to be 1.04 ± 0.04 eV. The derived activation energy barrier for the growth of the Ni germanide layer in the Ni/Zr-interlayer/Ge system was approximately 0.12 eV higher than that in the

Ni/Ge system. In the case of the Ni/Ta-interlayer/Ge system where the activation energy barrier is 0.21 eV higher than that in the Ni/Ge system, the high activation energy barrier can be attributed to the formation of a ternary amorphous layer that observed in the interface between the Ta-interlayer and the Ge substrate in the initial stages of the isothermal in situ annealing experiment (Lee et al., 2015). Thus, the higher activation energy barrier for the formation and growth of Ni germanide in the Ni/Ta-interlayer/Ge system was caused by the limited diffusion of Ni atoms through not only the Ta-interlayer, but also the ternary amorphous layer that remained between the Ta-interlayer and the newly formed Ni germanide layer.

For the Ni/Zr-interlayer/Ge system, on the other hand, no intermediate or intermixing layer between the Zr-interlayer and Ge substrate was formed in the ex situ (not shown) and in situ annealing experiments, and thus the Ni germanide was

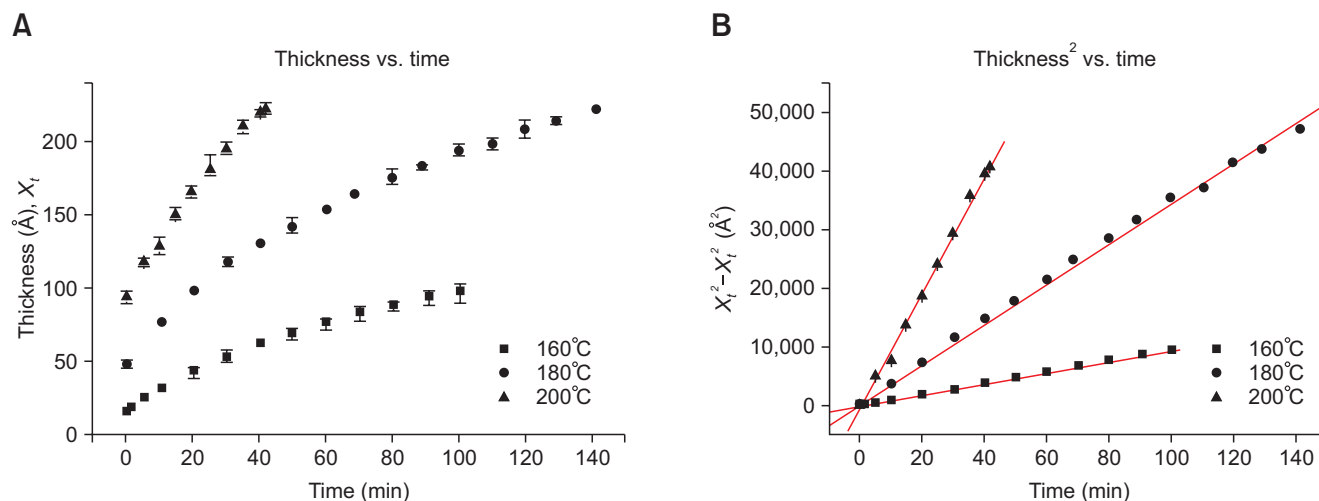


Fig. 5. Plots of the thickness of the Ni germanide layer in the Ni/Zr-interlayer/Ge system measured from the cross-sectional transmission electron microscopy micrographs as a function of the annealing time at three different temperatures of 160°C, 180°C, and 200°C. (A) Thickness versus time. (B) Thickness² versus time.

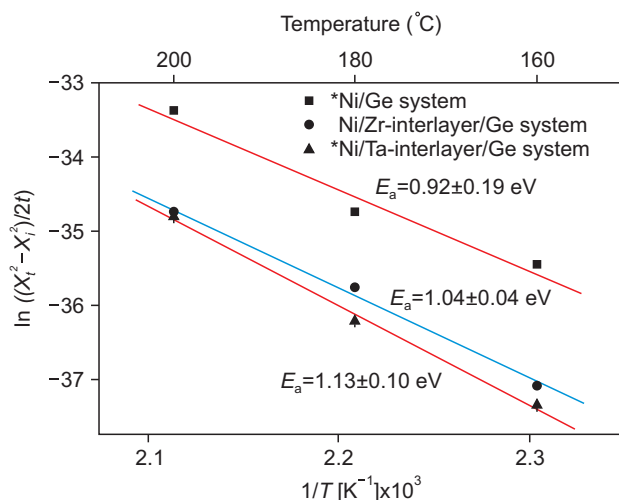


Fig. 6. Arrhenius plot of the growth rate of the Ni germanide layer in the Ni/Ge, Ni/Ta-interlayer/Ge and Ni/Zr-interlayer/Ge systems at three different temperatures of 160°C, 180°C, and 200°C. The activation energy for the Ni/Zr-interlayer/Ge system was calculated to be 1.04 ± 0.04 eV. *The data for Ni/Ge and Ni/Ta-interlayer/Ge systems obtained from Lee et al. (2015) (*Sci. Adv. Mater.* in print).

formed and grew uniformly due to Ni diffusion through the diffusion path created in the amorphous Zr-interlayer during the annealing process in the absence of any intermetallic compounds. Therefore, the activation energy for the growth of the Ni germanide layer in the Ni/Zr-interlayer/Ge system was slightly higher than that in the Ni/Ge system and a little lower than that in the Ni/Ta-interlayer/Ge system. However, in the previous in situ annealing experiments for the thick Zr-interlayer (>3 nm) (not shown), the germanidation reaction did not occur for temperatures up to 500°C. It is believed

that the formation of the Ni germanide was caused by the diffusion of Ni atoms through the Zr-interlayer, which is affected by the thickness of the Zr-interlayer. The process of the formation and growth of the Ni germanide in the Ni/Zr-interlayer/Ge system discussed above is briefly displayed in the schematic diagram shown in Fig. 7.

SUMMARY

This study examined the reaction kinetics of the growth of Ni germanide in the Ni/Zr-interlayer/Ge systems using isothermal in situ annealing in a TEM and compared with the Ni/Ge and Ni/Ta-interlayer/Ge systems. The reaction in the Ni/Zr-interlayer/Ge system was determined to be diffusion controlled with an activation energy of 1.04 ± 0.04 eV, and depended on the square root of the time. This value for the activation energy barrier is slightly higher than that of the Ni/Ge system and a little lower than that of the Ni/Ta-interlayer/Ge system. For the Ni/Ta-interlayer/Ge system, the increase in activation energy was due to the combination of the Ta-rich layer and the ternary amorphous layer formed in the initial stage of the annealing process. In contrast, the reaction kinetics in the Ni/Zr-interlayer/Ge system were affected only by the Zr-interlayer. This study demonstrates that the kinetic data points can be correlated with the microstructural change at each time in the in situ annealing TEM experiment.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

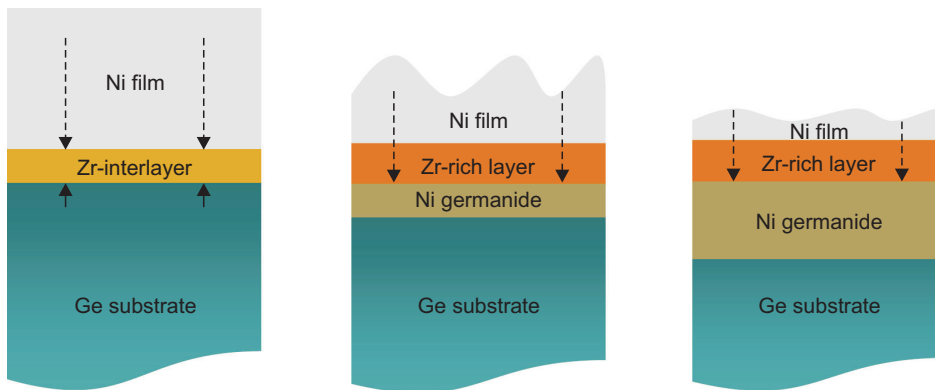


Fig. 7. Schematic diagrams of the process of the formation and growth of the Ni germanide in the Ni/Zr-interlayer/Ge systems.

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