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Temperature Calibration of a Specimen-heating Holder for Transmission Electron Microscopy

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The in-situ heating transmission electron microscopy experiment allows us to observe the time- and temperature-dependent dynamic processes in nanoscale materials by examining the same specimen. The temperature, which is a major experimental parameter, must be measured accurately during in-situ heating experiments. Therefore, calibrating the thermocouple readout of the heating holder prior to the experiment is essential. The calibration can be performed using reference materials whose phase-transformation (melting, oxidation, reduction, etc.) temperatures are well-established. In this study, the calibration experiment was performed with four reference materials, i.e., pure Sn, Al-95 wt%Zn eutectic alloy, NiO/carbon nanotube composite, and pure Al, and the calibration curve and formula were obtained. The thermocouple readout of the holder used in this study provided a reliable temperature value with a relative error of <4%.

Key Words: Melting point, Dynamic observation, Annealing, Thermocouple, In-situ transmission electron microscopy

INTRODUCTION

The electron microscope is capable of resolving crystal lattices and the resulting images can be interpreted from the viewpoint of atomic positions (Menter, 1956; Cowley & Iijima, 1972). As such, the use of high-resolution transmission electron microscopy (HR-TEM) has increased significantly, and HR-TEM has become an essential tool in material characterization. HR-TEM is especially effective in resolving nanoscale features, as is the case of various types of material interfaces (Holloway & Sinclair, 1987; Sinclair et al., 1989; Sinclair, 1990). However, like other ex-situ analysis techniques, HR-TEM is somewhat inadequate for the analysis of dynamic behavior, because the information is obtained from separate samples that undergo different processing. Therefore, determining the exact sequence of events during heating is sometimes difficult and tedious; important steps in the process may be missed, and the sequence may be completely misinterpreted. These problems are frequently encountered in the study of interfacial chemistry during dynamic reactions.

To facilitate dynamic observations, HR-TEM may be used in conjunction with in-situ heating of the sample inside the microscope. In-situ heating analysis is both unique and highly effective in making these observations and is therefore frequently combined with other types of characterization such as conventional TEM and X-ray diffraction (Glicksman & Schaefer, 1966; Glicksman & Vold, 1966; Butler & Hale, 1981; Raaijmakers et al., 1987; Beam & Chung, 1985). In-situ heating TEM has also been successfully used for the dynamic observation of atomic-scale events in experiments that employed a high-energy imaging electron beam for heating the sample (Hashimoto et al., 1980; Yamashita &

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Sinclair, 1983; Bovin & Smith, 1985; Eyring et al., 1985; Iijima & Ichihashi, 1986). These results are important for the study of the effect of electron-beam-induced heating, but differ significantly from those obtained with the actual thermal heating that occurs during material processing. Natural thermal heating of the sample is especially important for semiconductor materials that undergo several thermal cycles during device processing.

In order to produce experimental results by natural thermally activated processes, the sample must be heated externally in a holder with an embedded heating system, as successfully demonstrated by a number of research groups (Gibson et al., 1985; Sinclair et al., 1987; Sinclair et al., 1988; Smith et al., 1993). This was achieved despite the fact that heating holders were sometimes not sufficiently stable to allow HR-TEM image recording at elevated temperatures.

The temperature of the specimen, which is typically measured by a thermocouple during the annealing experiment, constitutes an important parameter in in-situ annealing experiments in a TEM. However, the thermocouple in the heated TEM holder is not in direct contact with the specimen, and hence the measured and actual temperatures of the region of interest in the sample, may differ. Measuring the actual temperature of the specimen during in-situ heating and determining the temperature dependence of the dynamic reactions is therefore essential. This can be achieved by performing a calibration experiment with standard specimens prior to the in-situ heating experiment. This article briefly reviews various methods of temperature calibration for a specimen-heating holder. The procedure and result of the temperature calibration experiment, performed on pure elements (Sn and Al) and NiO/carbon nanotube (CNT) composites, is described.

MATERIALS AND METHODS

The in-situ annealing experiments were performed at 300 kV in a JEOL-3011 (JEOL Co., Ltd., Japan) equipped with a LaB_6 filament. Fig. 1 shows the setup used for the in-situ annealing

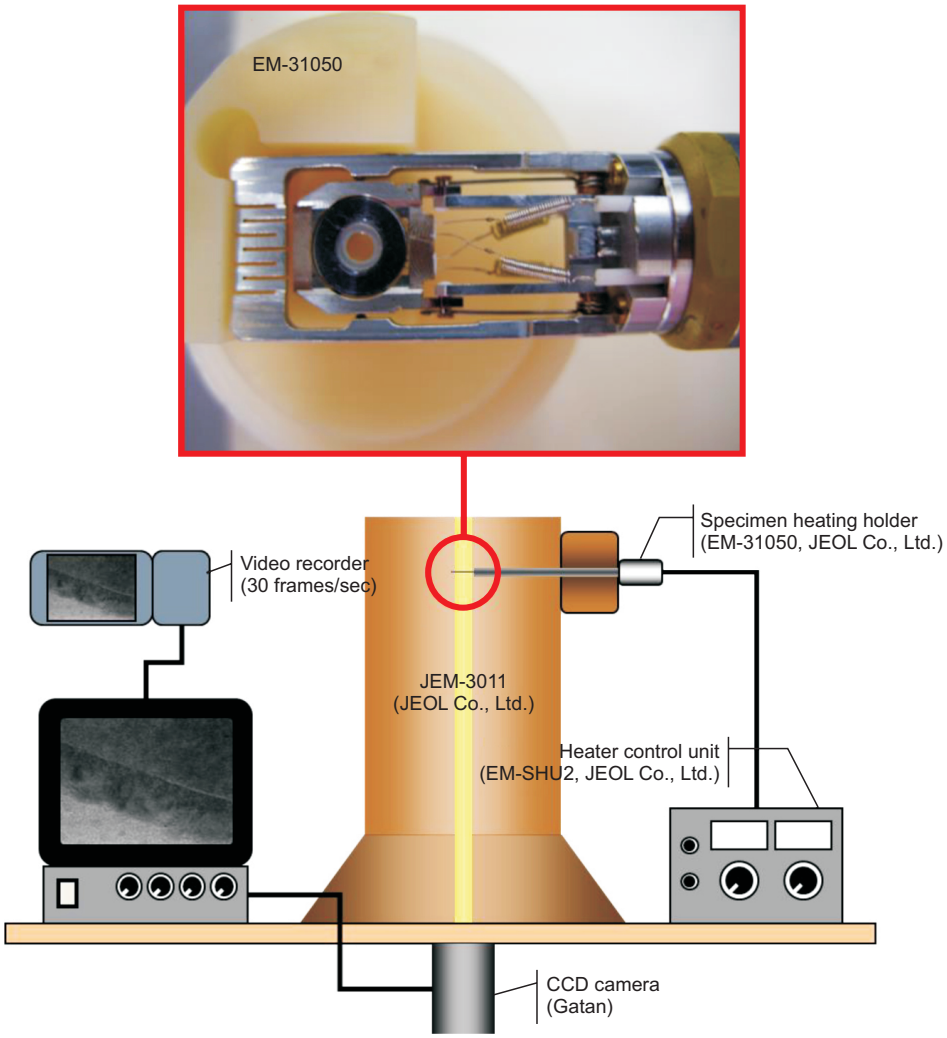

Fig. 1. Schematic of the in-situ annealing and recording system equipped with a JEOL EM-31050 (JEOL Co., Ltd., Japan) specimen-heating double-tilting holder. CCD, charge-coupled device.

experiments. A model EM-31050 JEOL heating holder (JEOL Co., Ltd.) equipped with a Pt/Pt-13%Rh thermocouple in contact with the furnace was used to resistively heat the specimens and measure the temperature of the specimen up to 900°C. In addition to normal photographic recording, images from a Gatan 622 TV rate camera system (Gatan, USA) were recorded on video tape at a time resolution of 30 frames per second (fps). Most of the images were extracted from video tapes recorded at different stages of the experiments; figures taken from the video recording are identified by the descriptions in the captions.

RESULTS AND DISCUSSION

As previously mentioned, the thermocouple of the specimen-heating holder is typically in direct contact with the furnace and not with the specimen; determining the temperature difference between the measured and actual temperature values of the area of interest in the TEM specimen is essential. Several methods for calibrating the temperature of the specimen-heating holder have been reported. These include:

Solid-phase Epitaxial Regrowth

When annealed, ion-implanted amorphized surface layers of Si and Ge crystallize via the movement of the sharp crystal/amorphous interface toward the free surface. The thickness of the epitaxially crystallized layer increases with time at a given temperature resulting eventually in a single-crystal epitaxial film. The corresponding growth rates are well-described by an Arrhenius dependence on temperature, with activation energies of 2.70 and 2.00 eV for Si and Ge, respectively. The effects of dopants and ion irradiation on the growth process in Si have also been extensively studied (Olson & Roth, 1988). Stach et al. (1998) investigated the temperature calibration of the TEM heating holder using a combination of solid-phase epitaxial regrowth and the focused ion beam sample preparation technique. They carefully examined the regrowth region from a sample annealed for 30 min at a thermocouple reading of 575°C. The measured regrowth velocity for this sample was 4.4 nm/sec, which indicates that the thermocouple reading was highly accurate in this case. Interestingly, the thermocouple readout on the other heating holder used in their laboratory was consistently 25°C lower than the actual temperature determined from the regrowth experiments performed on amorphous Si. This emphasizes the importance of carefully calibrating individual holder.

Metal-Mediated Crystallization

Early studies on amorphous Si showed that the crystallization temperature of Si is significantly reduced when metal contacts are used. This phenomenon, referred to as metal-catalyzed or metal-mediated crystallization (MMC), has been extensively studied in Ge/metal and Si/metal systems.
Sinclair and Konno (1994) showed that the MMC of Ge in Ag-Ge multilayers occurs at a temperature of 270°C~280°C, which is ~240°C lower than that of pure amorphous Ge. Their observations indicated that Ge atoms from the amorphous phase diffused through the Ag grains and precipitated onto the crystalline phase. They also described in-situ high-resolution electron microscopy of the MMC of semiconductors, particularly for the Ag-Ge and Ag-Si systems. More importantly, the kinetics, thermodynamics, and in-situ observations were mutually consistent. Hence, the in-situ crystallization reaction occurred at the same temperature as that of the exothermic reaction peak observed in the results of calorimetry measurements. This crystallization reaction can therefore be used as a reference to calibrate the thermocouple readout on the heating holder.

Melting Point Measurement

Standard materials with accurately determined solid?liquid phase transition temperatures (melting points) can be used for the calibration. Melting begins at the edge of the sample and proceeds to the interior. In addition, thickness contours that occur at heating temperatures up to the melting point, allow easy identification of the solid-liquid interface.
Kang (2009) examined the melting behavior of the Sn-3.5Ag (T_m=222°C) alloy with increasing temperature from room temperature to 190°C (the temperature indicated by the heating controller). The alloy began melting at a lower temperature (~170°C) than the established melting temperature. This suggests that the actual specimen temperature is higher than that indicated by the thermocouple readout. The temperature difference between the TEM specimen and the thermocouple readout was found to be ~50°C.

Direct Temperature Measurement

The temperature of the heating holder can be measured by a pyrometer, which is a non-contact device that intercepts and measures thermal radiation in a process referred to as pyrometry. A pyrometer has an optical system and a detector and hence temperature measurements must be performed in a specially designed vacuum chamber. Using this chamber, Lee (2006) obtained a calibration curve for the temperature of graphite flakes by performing a series of heating experiments with a tungsten filament (heating element). During the experiments, the temperature of the filament was measured by monitoring the melting of pure substances such as Sn and Au. Pyrometers (MINOLTA IR-308, TR-630A; Minolta, Japan) were used to complete the calibration for measurements at temperatures of 300°C~2,000°C. The results of these measurements revealed that the temperature of the graphite flake (substrate) differed only slightly from that of the filament.

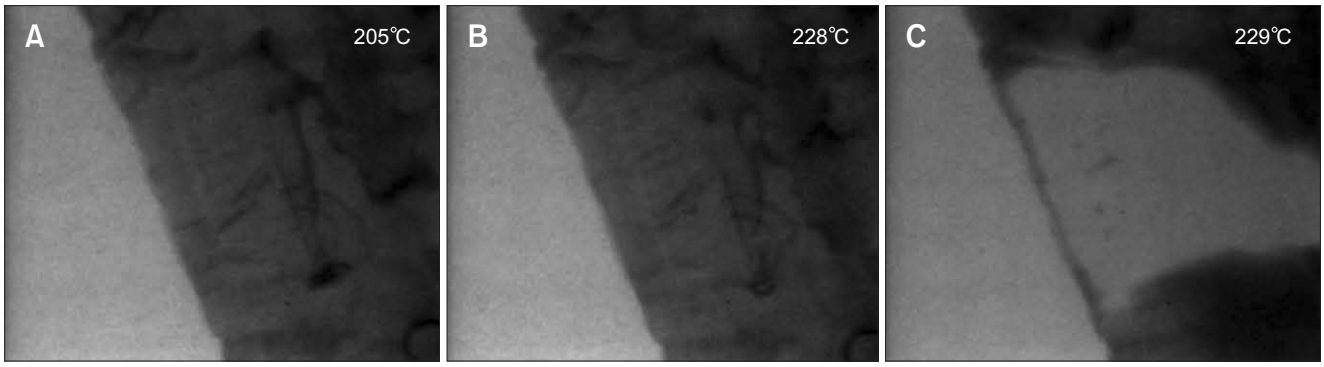

Fig. 2. Individual frames digitized from a video sequence recorded using pure Sn during annealing at temperatures ranging from room temperature to 229°C.

Temperature Calibration for Our Specimen Heating Holder

In order to obtain the temperature calibration curve, the calibration experiment was performed with four specimens namely, pure Sn, Al-95 wt%Zn eutectic alloy, NiO/CNT composite, and pure Al (listed in the order of target temperature to be calibrated).

Pure Sn with a known melting temperature of ~231°C, can be used in the low-temperature range of the melting point measurement method. The specimen was heated from room temperature to 230°C (the temperature indicated by the heating controller) and was abruptly transformed at 229°C, from a crystalline solid into an amorphous liquid. Fig. 2 shows that the pure Sn starts to melt at 229°C, indicated by the thermocouple readout, which is slightly lower than the known melting temperature (231°C). This result demonstrates that the temperatures of the TEM specimen and the thermocouple readout on the heating controller are almost the same in the low-temperature regime. However, the temperatures deviate appreciably with increasing temperature, as observed in the in-situ heating experiment performed on an Al-95 wt%Zn eutectic alloy, whose melting point is 382°C. In that case, the thermocouple readout was 7°C lower than the actual temperature of the specimen (the melting temperature of the alloy).

At intermediate temperatures of ~500°C, a nano-composite in which NiO nanoparticles are attached to a CNT can be used as an effective calibration standard. Fig. 3A shows the results of thermo-gravimetric analysis of two NiO/CNT nano-composites with different NiO contents. Both samples exhibited weight losses, and peaks occurred in the derivative thermo-gravimetric (DTG) plots at ~530°C. Moreover, the oxygen in the NiO constituted the only source for oxidizing the CNTs. Therefore, the CNTs were oxidized at the interface between the NiO and CNT by consuming oxygen from NiO, reducing NiO to Ni at the peak temperature of the DTG plots. The temperature at which the NiO→Ni phase transition occurs is measured by using a TEM to observe the dynamic changes in the diffraction patterns of NiO. At 500°C on the

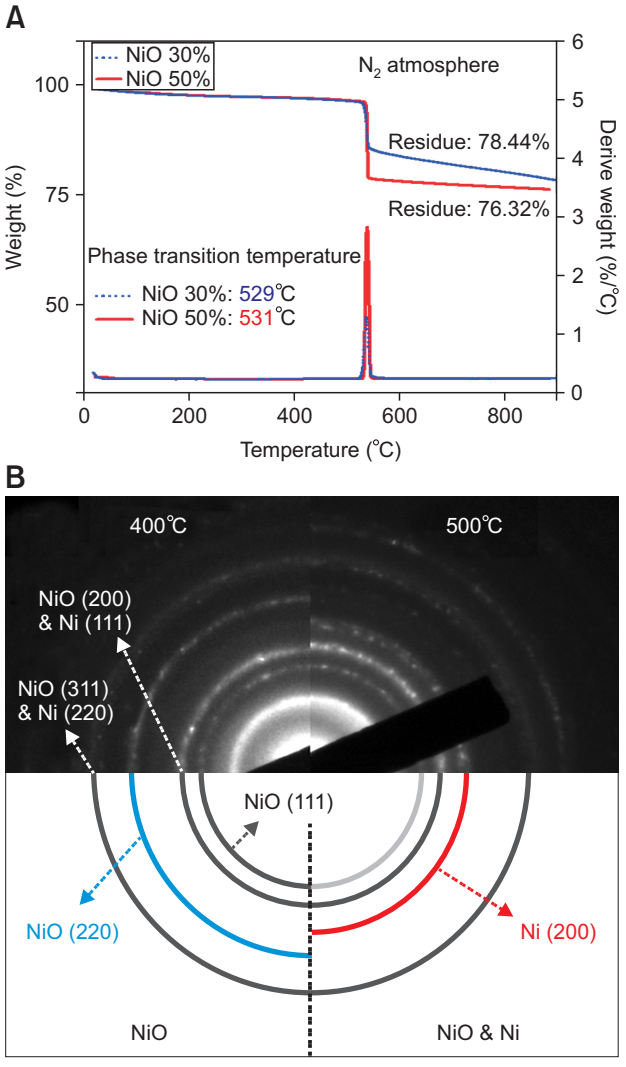

Fig. 3. (A) Results from the thermo-gravimetric analysis analysis of NiO/carbon nanotube composite under N_2 atmosphere demonstrate that the phase transition (NiO→Ni) occurs at 530°C. (B) Dynamic change in selected area diffraction patterns during the in-situ heat-treatment performed inside the transmission electron microscopy. The left and right patterns obtained at 400°C and 500°C consist of diffraction rings corresponding to NiO and Ni, respectively.

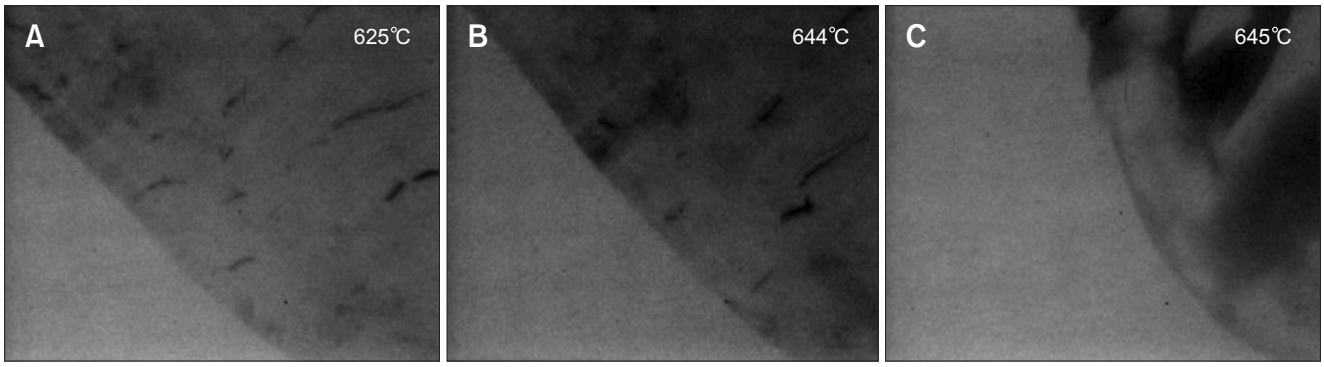

Fig. 4. Individual frames digitized from a video sequence recorded using pure Al during annealing at temperatures ranging from room temperature to 645°C.

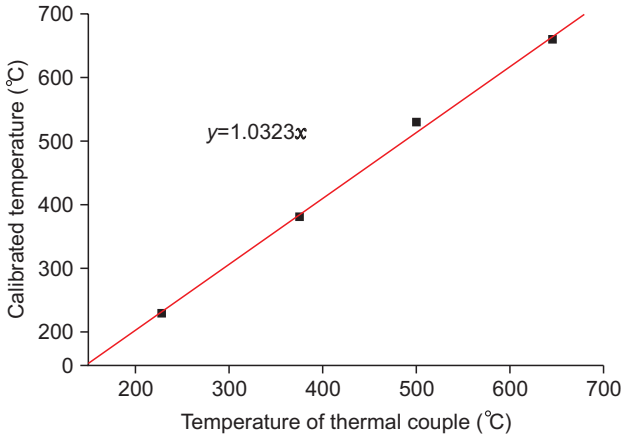

Fig. 5. The calibration curve and fitting formula of the thermocouple readout vs. calibrated temperature.

thermocouple readout, the intensity of the (111) and (220) planes of NiO decreased while the (200) plane of Ni appeared in the selected area diffraction patterns (Fig. 3B). This result indicates that the temperature of the TEM specimen and the heating controller differ by ~30°C in the intermediate temperature range.

Pure Al (T_m=660°C) is suitable for measurements performed in the high-temperature range. Like pure Sn, pure Al was heated to its melting temperature and the solid phase of the specimen was transformed to liquid (Fig. 4) at a measured temperature of 645°C. Therefore, the actual temperature of the specimen is 15°C lower than the indicated temperature of the heating controller.

We produced a thermocouple temperature versus calibrated temperature curve from the experimental data (Fig. 5); this curve was described by a first-degree polynomial (i.e., linear equation) of the form y=ax+b. Based on the calibration curve and formula, the actual temperature was related to the thermocouple readout as follows: actual temperature=1.0323×thermocouple readout. Therefore, the thermocouple readout temperature can be used to estimate the actual temperature of the specimen. However, this relation is not universal, and therefore each holder should be carefully calibrated.

SUMMARY

In-situ annealing in TEM allows direct observation of dynamic processes occurring in materials on nanoscale. The method allows individual events to be thoroughly analyzed, enabling direct and precise measurements. The in-situ heating TEM experiment allows us to unambiguously observe the time- and temperature-dependent dynamic reactions of the same specimen. The temperature is a major experimental parameter and must be measured accurately during in-situ heating experiments. Therefore, the thermocouple readout of the heating holder must be calibrated prior to the in-situ heating experiment. This calibration can be performed with reference materials that have well-established phase transformation (melting, oxidation, reduction, etc.) temperatures.

In this study, the calibration experiment was performed with four specimens namely, pure Sn, Al-95 wt%Zn eutectic alloy, NiO/CNT composite, and pure Al (listed in the order of which the temperature, calibration curve, and formula were obtained). The thermocouple readout of the holder used in this study provided a reliable temperature value with a relative error of <4%.

CONFLICT OF INTEREST

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

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