Development of Unique Specimen Holder for LEED-AES Study at High Temperatures

S. Iida,* T. Tsujita, T. Nagatomi and Y. Takai
Department of Material and Life Science, Gradate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

**iida@ap.eng.osaka-u.ac.jp*

(Received November 8, 2001; Accepted February 7, 2002)

A unique specimen holder for LEED (low energy electron diffraction) and AES (Auger electron spectroscopy) study at high temperatures has been developed with considerable success. It enables us to observe the LEED pattern of a clean W(100) surface with enough contrast using a commercial-type LEED system at 1400 K. AES spectrum for the W(100) surface at 1400 K has been successfully measured without any effects caused by the heating of the specimen. The present result leads us to the confirmation that the developed specimen holder is well worthy to be applied to the systematic study of the Sc-O/W(100) system at high temperatures.

Introduction

A Sc-O/W(100) Schottky emitter has been recently attracting much attention because of its potentiality as another promising emitter as a Zr-O/W(100) which has been widely used in practice. Nishiyama *et al.* [1] have first reported superior properties of electron emission of the Sc-O/W(100) Schottky emitter as follows:

(i) An operating temperature of the Sc-O/W(100) emitter is lower than that of the Zr-O/W(100), leading to an energy width of emitted electrons of only ~0.25 eV.

(ii) The angular current density is as high and stable as those of the Zr-O/W(100) Schottky emitter.

For accommodating a practical use of the Sc-O/W(100) Schottky emitter, surface properties of the Sc-O/W(100) emitter are to be elucidated.

Although the role of Sc_2O_3 in a scandate cathodes [2] and Sc_2O_3 dispersed oxide cathodes [3] for a cathode ray tube has been studied to some extent, the study on the Sc-O/W(100) Schottky emitter is, to our knowledge, very limited. Kultashev and Makarov [4] have investigated the Sc-O/W system and found the preferential decrease in the work function for the W(100) surface by heating at ~1100K. They have speculated that penetration of oxygen atoms to beneath the topmost scandium atoms causes marked decrease of the work function. Zagwijn *et al.* [5] have studied effects of the scandium and oxygen in the scandate dispenser cathodes and found the scandium-oxygen overlayer decreases the work function of the W(100) surface even at the room temperature.

With respect to the Sc-O/W(100) Schottky emitter, Kawano *et al.* [6,7] have first systematically studied the Sc-O/W(100) surface using the methods based on the surface characterization as performed by Danielson and Swanson [8] and by Shimizu and coworkers [9-11] for the Zr-O/W(100) system. Their results strongly suggested that Sc-O complexes are formed on the W(100) surface by the oxygen atoms locating beneath the topmost scandium atom, resulting in the marked reduction of the work function. For more comprehensive understanding of the mechanism of the reduction of the work function in the Sc-O/W(100) system, information on the atomic arrangement at the Sc-O/W(100) surface at the operating temperature is to be obtained.

From practical point of view, a LEED (low energy electron diffraction) and RHEED (reflection high energy electron diffraction) techniques have been widely used for the structural analysis of the surface. An energy of incident electrons in the RHEED technique is much higher than that in the LEED and a distance between the specimen and the observation screen is much longer in the RHEED system than that in the LEED. These characteristics enable the RHEED technique to be employed for the observation of the diffraction pattern at the high temperatures in some studies [11-13]. However, the LEED technique has a advantages compared to the RHEED as follows; the LEED pattern provides the information on the two dimensional reciprocal lattice at once and three dimensional information is to be obtained by only changing the incident energy. In this regard, the study of the surface atomic arrangement using the LEED technique should be more informative than that by the RHEED.

In the present study, therefore, we aim at a development of a unique specimen holder to perform both a LEED observation using a conventional LEED system and an AES (Auger electron spectroscopy) measurement at the operating temperature of the Sc-O/W(100) Schottky emitter of ~1400 K.

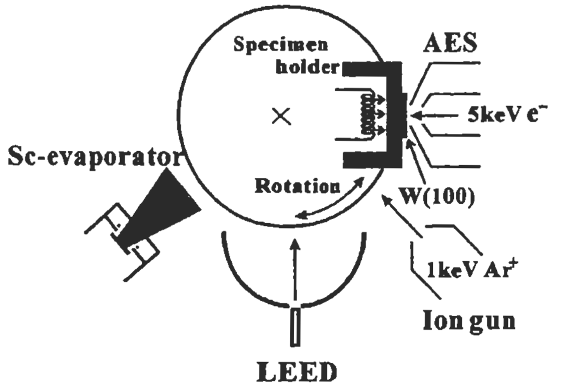

Fig. 1 The schematic illustration of the experimental apparatus, scanning Auger microscope (SAM-545, Physical Electronics Industries). The apparatus equipped with the ion gun for the sputtering, the commercial-type LEED system and the laboratory-made Sc-evaporator. The developed specimen holder can be rotated for the LEED, AES, ion sputtering and Sc-evaporation. The base pressure of the apparatus is ~2.0×10^{-10} Torr.

Specimen holder

Figure 1 shows the schematic illustration of the experimental apparatus, scanning Auger microscope (SAM-545, Physical Electronics Industries). The apparatus equipped with an ion gun for sputter cleaning, the commercial-type LEED system (ELD-1000RV, EIKO) and a laboratory-made Goto-type [6,14,15] Sc-evaporator. The developed specimen holder can be rotated for the LEED, AES, sputter cleaning and Sc-evaporation. The base pressure of the apparatus is ~2.0×10^{-10} Torr. The primary energy of the electrons for the AES measurement was 5 keV. The LEED observation was performed using 40 eV electrons. The 1 keV Ar^+ ions were used for the sputter cleaning.

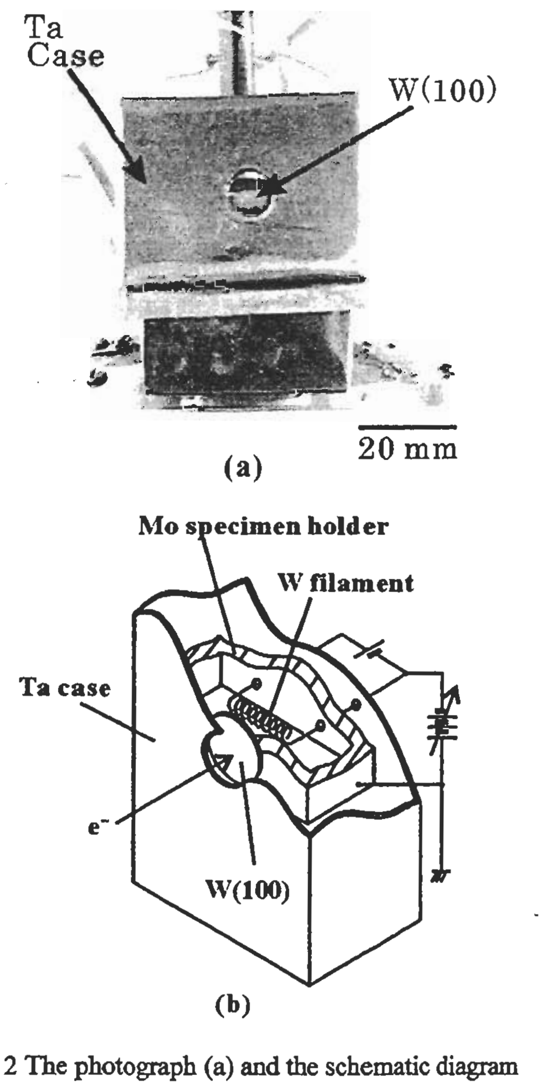

Fig. 2 The photograph (a) and the schematic diagram (b) of the developed specimen holder.

The photograph and schematic diagram of the developed specimen holder are depicted in Figs. 2(a) and (b), respectively. The specimen of the W(100) disk (ϕ9 mm×1 mm) is directly welded on the Mo block in order to obtain good thermal contact between the W(100) specimen and Mo block. The W filament for heating is located inside the Mo block. The specimen is heated by the electron bombardment. The Mo block works as a heat bath and enables the temperature of the specimen to be stable. Setting the W filament inside the Mo block prevents the electrons emitted from the W filament, of which the energy is more than a few hundreds eV during the heating, from going into the LEED screen or the CMA (cylindrical mirror analyzer) for the AES measurement. The temperature of the specimen is monitored by the electric power used for heating as described bellow. The Mo block is covered by a Ta case in order to reduce the light emitted from the holder at the high temperatures irradiating the LEED screen during the LEED observation. The Ta case has an aperture of ϕ7 mm in front of the specimen for the LEED and AES.

Figure 3(a) show the temperature of the specimen surface as a function of the electric power used for heating by the electron bombardment. The electric power for heating is defined as the product of the emission current from the W filament, I_e, and the voltage applied between the W filament and Mo block, V_{heat} (see Fig. 3(b)). In the present study V_{heat} was set at -350 V. The temperature was measured by an optical pyrometer (IR-AP, CHINO). The circler, rectangular and triangular marks correspond to each set of the measurement. The solid and open marks represent the temperature measured while the electric power is increased and decreased, respectively. From Fig. 3(a), it is confirmed that the reproducibility of the temperature is within ±15 K and the specimen can be heated up to ~1900 K. Note that the temperature required for flashing of the W surface is ~1800 K.

Figure 4 plots the result of the measurement of the stability of the temperature with the passage of time for 60 min. The temperature was set at 1400 K corresponding to the operating temperature of the Sc-O/W(100) Schottky emitter. The electric power for heating was 44.6 W. It is found that the stability at the operating temperature is ±1 K /hour, leading us to the confirmation that the stability of the Sc-O/W(100) surface in the long term is to be measured.

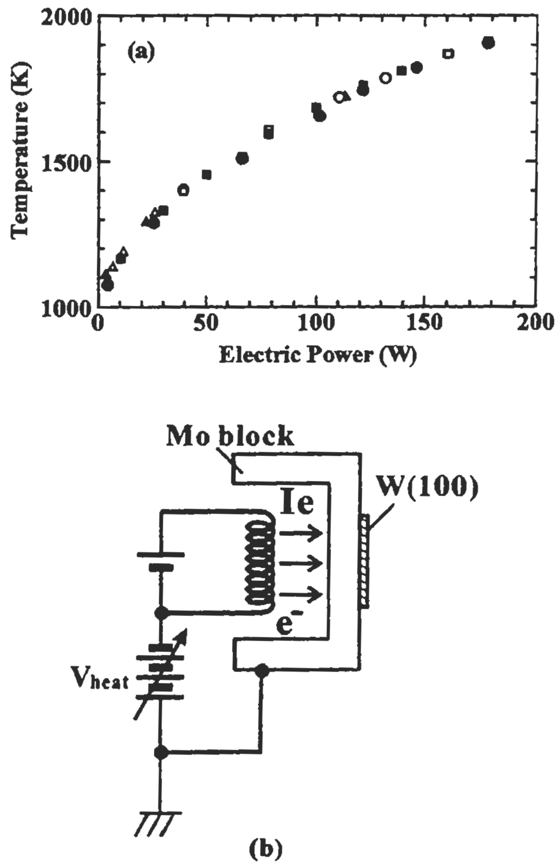

Fig. 3 The temperature of the specimen surface as a function of the electric power used for heating by the electron bombardment (a) and the schematic illustration of heating by the electron bombardment (b). The electric power for heating is defined as the product of the emission current from the W filament, I_e, and the voltage applied between the W filament and Mo block, V_{heat}. In (a), the circler, rectangular and triangular marks correspond to each set of the measurement. The solid and open marks represent the temperature measured while the electric power is increased and decreased, respectively.

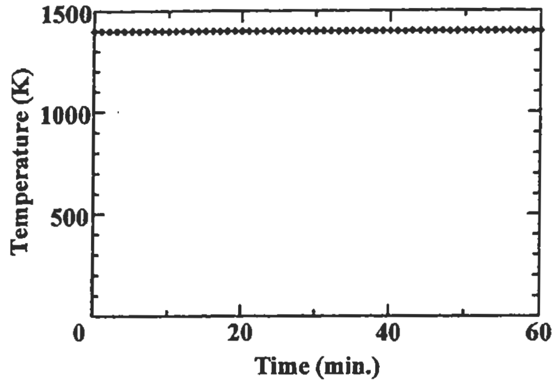

Fig. 4 The stability of the temperature with the passage of time for 60 min. The temperature was set at 1400 K corresponding to the operating temperature of the Sc-O/W(100) Schottky emitter. The electric power for heating was 44.6 W. The stability at the operating temperature is ±1 K /hour.

LEED observation and AES measurement of clean W(100) surface at high temperatures

In order to confirm whether or not the new specimen holder is applicable to the study of the Sc-O/W(100) system, the LEED observation and AES measurement were performed for the clean W(100) surface at high temperatures. The as-received specimen of the mechanically polished W(100) disk (Rare Metallic, Japan) was first electrochemically etched using NaOH solution (2.4 mol/ℓ) to remove the heavy carbon-contaminants on the surface, which is considered to be introduced by diamond powders during the mechanical polishing. Then, the W(100) specimen was attached to the specimen holder and introduced to the apparatus. The cleaning of the W(100) surface was performed by repetition of the sputter cleaning and flashing at ~1900 K until no AES peaks of the contaminants were visible except for oxygen. In the case that the carbon-contaminants were not removed by the sputtering-annealing procedure, the specimen was heated at ~1900 K in oxygen atmosphere of $\sim 1\times10^{-6}$ Torr during the sputter cleaning. The heating of the specimen at 1400 and 1900 K deteriorated the pressure of the apparatus to $\sim 1\times10^{-9}$ and $\sim 5\times10^{-9}$ Torr, respectively. The LEED pattern was recorded by the digital still camera (DSC-D700, Sony). For the improvement of the contrast of the recorded LEED patterns, the red component of the recorded images due to the black body radiation from the specimen surface is cut by filtering using the digital image processing. All images are processed in the same manner.

Figure 5 shows a series of the LEED patterns observed at the high temperatures for the clean W(100) surface. Figs. 5(a) to (d) depict the LEED patterns obtained at the room temperature, 1200, 1300 and 1400 K, respectively. The LEED pattern at the room temperature in Fig. 5(a) shows a sharp (1×1) pattern from the clean W(100) surface. The (1×1) pattern is clearly visible even at 1400 K in Fig. 5(d). Although the contrast is getting lower from (a) to (d) because of the background due to the light from the specimen surface, the contrast of the LEED pattern in Fig. 5(d) is still enough to observe the pattern clearly at 1400 K. These results of the LEED observation at high temperatures lead us to the confirmation that the new specimen holder is well worthy to be applied to the study of the Sc-O/W(100) surface at its operating temperature of 1400 K.

Figure 6 shows the AES spectra of the W(100) surface measured in order to confirm whether or not the acquisition of the AES

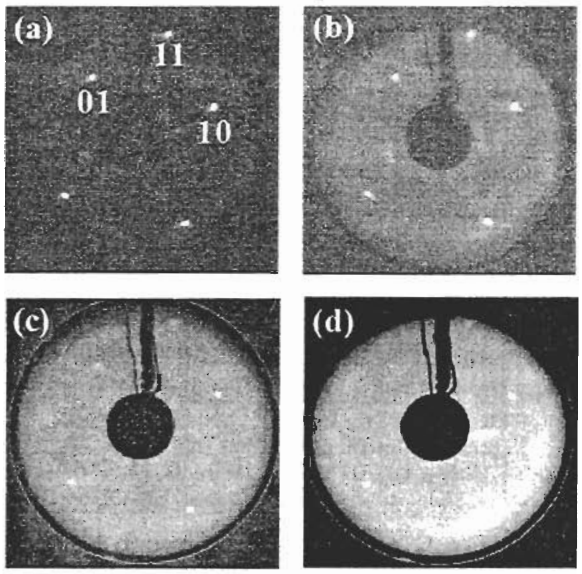

Fig. 5 A series of the LEED patterns observed for the clean W(100) surface using the new specimen holder at various temperatures. The temperatures are (a) the room temperature, (b) 1200, (c) 1300 and (d) 1400 K, respectively.

spectrum can be performed at high temperatures. Figure 6(a) depicts the AES spectrum measured at the room temperature for the W(100) surface before cleaning of the surface. The AES peaks due to the contaminants of carbon, nitrogen and oxygen are seen. After the measurement of the AES spectrum in Fig. 6(a), the specimen was heated to 1400 K. The AES spectrum of the W(100) surface measured at this stage is plotted in Fig. 6(b). Comparing the AES spectra in Figs. 6(a) and (b), the AES peaks of the contaminants disappear except for a small peak of oxygen. From Fig. 6(b), it is found that the voltage of -350 V applied to the W filament and the electrons emitted from the W filament do not affect the AES spectrum at all, leading to the confirmation that the surface composition and bonding state at 1400 K can be qualitatively studied by AES.

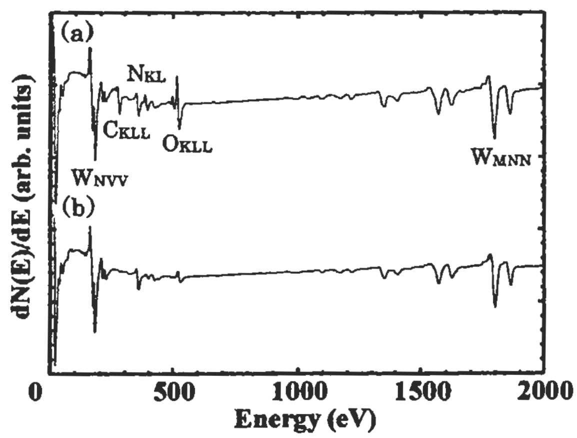

Fig. 6 The AES spectra of the W(100) surface. (a) the spectrum measured at the room temperature before the cleaning of the specimen surface. (b) the spectrum measured at 1400 K by heating the specimen after the measurement of the spectrum in (a).

Conclusions

In the present study, the specimen holder for the LEED observation and AES measurement at the high temperature of ~1400 K has been developed with considerable success. The present results are summarized as follows:

(1) The LEED pattern from the W(100) surface is clearly observed even at 1400 K with enough contrast using the commercial-type LEED system by combining with the digital image processing.

(2) The AES spectrum is successfully measured at 1400 K without any effects of heating the specimen.

Consequently, it is confirmed that the developed specimen holder is well worthy to be applied to the LEED-AES study of the Sc-O/W(100) surface at high temperatures. Further study of the Sc-O/W(100) surface at high temperature is under the investigation.

References

[1] H. Nishiyama, T. Ohshima and H. Shinada, Appl. Surf. Sci. **146**, 382 (1999).

[2] S. Yamamoto, S. Taguchi, I. Watanabe and S. Kawase, Jpn. J. Appl. Phys. **25**, 971 (1986).

[3] M. Saito, R. Suzuki, K. Fukuyama, K. Watanabe, K. Sano and H. Nakanishi, IEEE Trans. Electron Devices **37**, 2605 (1970).

[4] O.K. Kultashev and A.P. Makarov, Bull. Acad. Sci. USSR, Phys. Ser. **35**, 321 (1971).

[5] P.M. Zagwijn, F.W.M. Frenken, U. van Slooten and P.A. Duine, Appl. Surf. Sci. **111**, 35 (1997).

[6] T. Kawano, T. Saito, Y. Takai and R. Shimizu, Surf. Interface Anal. **27**, 981 (1999).

[7] T. Kawano, Y. Takai and R. Shimizu, Jpn. J. Appl. Phys. **39**, 577 (2000).

[8] L.R. Danielson and L.W. Swanson, Surf. Sci. **88**, 14 (1979).

[9] R. Shimizu, J. Electron Microsc. **47**, 371 (1998).

[10] S.C. Lee, Y. Irokawa, M. Inoue and R. Shimizu, Surf. Sci. **330**, 289 (1995).
[11] Y. Irokawa, R. Mitsuhashi, S.C. Lee, Y. Kimura, M. Inoue, Y. Takai and R. Shimizu, Surf. Sci., **367**, 96 (1996).
[12] Y. Irokawa, R. Mitsuhashi, S.C. Lee, K.Y. Min, M. Inoue, Y. Kimura and R. Shimizu, Jpn. J. Appl. Phys. **35**, 4042 (1996).
[13] T. Kawano, T. Saito, Y. Takai and R. Shimizu, Jpn. J. Appl. Phys. **38**, 2951 (1999).
[14] K. Goto, T. Koshikawa, K. Ishikawa and R. Shimizu, J. Vac. Sci. Technol. **15**, 1695 (1978).
[15] Y.W. Beag, K. Egawa and R. Shimizu, Rev. Sci. Instrum. **64**, 3647 (1993).

Reviewer's comments

Reviewer: Hideki Yoshikawa (NIMS)

Questions:

Q1) The thermal contact between a Mo block and W(100) specimen should be an important point in order to obtain high specimen temperature. If you contrived it, tell how to get good thermal contact, please.

A1) In order to obtain the good thermal contact between the Mo block and W(100) specimen, the W(100) specimen was directly welded on the Mo block. In the experiment, it was confirmed that the temperatures of the surface of the W(100) specimen and Mo block are the same within the accuracy of the optical pyrometer. In addition to the thermal contact, this configuration enables the specimen temperature to be controlled by the electric power for heating with high reproducibility as mentioned in the text at Fig. 3(a). According to the referee's comments, we added the sentences describing this point in the text (3 th line in the left column of page 3).

Q2) You mentioned that the contrast is getting lower at higher temperature because of the background due to the light from the specimen surface. Can it be concluded that broad pattern at higher temperature is not including the real LEED contrast like a diffuse scattering pattern?

A2) It is impossible to conclude that there is no contribution of the real LEED contrast like the thermal diffuse scattering to the LEED pattern observed at 1400 K in Fig. 5(d). Although the LEED pattern in Fig. 5(d) would include the effects of both the real LEED contrast and the light emitted from the specimen, the contribution of the light is significant in our experiment. However, it could provide us useful information on this point to perform subtraction between two images in which one is taken with the incident electron on and the other off.

Reviewer: Toshio Urano (Kobe University)

高温（～1400 K）における金属試料のLEED-AES 測定のための試料ホルダーの試作に関する興味深い知見を述べており、掲載に値すると思います。
以下の点について御検討いただければ幸いです。

Comments:

C1) 試作の目的は Sc-O/W(100) Schottky emitter の動作状態での LEED-AES 測定を目指したものですが、この論文では W(100) clean surface の測定しか示されていません。従って、タイトルを含め Sc-O/W(100) の字句があまりに多数出現することに違和感を感じます。目的に関わる Introduction の項以外は大幅に削除するか、単に”高温における測定のための”などのように改めるべきと思います。たとえば、タイトル中、アブストラクト中の１つ目と３つ目、２ページの左列の最終行か右列の行目、３ページ右列９行目、４ページ左列６行目、４ページ右列２６行目か２７行目、５ページ左列２３行目、５ページ右列６行目、など。

A1) 御指摘ありがとうございました。
Sc-O/W(100)を含む字句について、以下の通り旧原稿中 8 ヶ所を削除致しました。
1 ページ：タイトル、
アブストラクト 2 行目・4 行目
2 ページ：左列最終行、右列 3 行目
4 ページ：右列最終行
5 ページ：左列 23 行目、右列 6 行目

C2) "developped specimen holder"もくどいように思います。大部分は new specimen holder とするか、単に specimen holder として良いのではないかと思います。たとえば、３ページ左列４行目、右列１０行目、４ページ左列５行目、１７行目、右列９行目、２４行目、５ページ左列５行目、２５行目、など。

A2) "developed specimen holder"についても以下の通り、訂正、削除致しました。
削除
3 ページ：右列最終行
4 ページ：右列 9 行目
5 ページ：左列 5 行目・最終行
書き換え
4 ページ：左列 5 行目・17 行目、右列 24 行目、図 5 のフィギュアキャプション中

C3) ３ページ左列２６行目と右列１行目の温度測定の記述がだぶっています。

A3) 温度測定の記述について、旧原稿中 3 ページ左列最終行からの一文を削除致しました。

C4) ４ページ左列２０行目"reputation" は "repetition" でしょうか？

A4) "reputation"を、"repetition"に訂正致しました。