Experiments for improving fabrication, recovery and surface-protection of Cs₃Sb photocathode

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Abstract

We examined 1) the photocurrent from Cs₃Sb photocathode as a function of anode voltage below 200 V, 2) the relationship between the quantum efficiency of photoemission and the conditions for fabrication by the sandwich method, 3) recovery of the photoemission by additional Cs deposition, and 4) the effects of surface protection of Cs₃Sb photocathodes by WO₃ and Cr₂O₃ films in the passive state. The photocurrent had a maximum at approximately 68 V except when we increased the anode voltage extraordinarily slowly. Cs₃Sb photocathodes were fabricated by increasing the temperature of sandwiched layers of Sb, Cs and Sb deposited on the fine tips of eight cathodes at less than -12°C. Cs₃Sb photocathodes having higher quantum efficiency were fabricated by smoothly increasing the temperature of the layers quickly after we deposited the second Sb layer. The photocurrent from the Cs₃Sb photocathodes was significantly higher when Cs was deposited at temperatures of 50–70°C. Deposition of a one- to three- atomic-layer W or Cr film extended the photoemission lifetime after the layers were oxidized to WO₃ or Cr₂O₃ in the passive state due to oxidation. The WO₃ or Cr₂O₃ in the passive state provided more surface protection as their thickness increased.

1. Introduction

Several photoemissive materials have extremely high quantum efficiency in the visible light region. For instance, the quantum efficiency of Cs₃Sb is approximately

11% at a wavelength of 405 nm, and 4.5% at 488 nm [1]. The quantum efficiency is generally defined as the ratio of the number of photoelectrons emitted via the photoelectric effect to the number of incident photons times 100. A cathode tip coated with Cs₃Sb can emit photoelectrons with a current of approximately 18 mA and initial kinetic energies lower than 2.54 eV if it is irradiated by a laser with a wavelength of 488 nm and an intensity of 1 W. In comparison, the electron beam current in a transmission electron microscope (TEM), where the initial energy spread of the electron beam should be as small as possible, is usually approximately 50 μ A for a LaB₆ thermal-type electron source, and 5–20 μ A for a cold-field emission-type source [2]. Therefore, the electron current from laser-irradiated Cs₃Sb could be much larger than those from the usual electron sources for TEMs. Because the quantum efficiencies of photocathodes of K₃Sb, Rb₃Sb, Na₂KSb, (Cs)Na₂KSb, K₂CsSb, Cs₂Te, GaAs(Cs), and so on are of the same order of magnitude as that of a Cs₃Sb photocathode in the visible region [3], a cathode tip coated with one of these photoemissive materials could be an extremely high-intensity electron source for TEMs.

Because a higher-intensity electron source improves the performance of a TEM, a photocathode coated with one of these photoemissive materials could provide a better electron source for TEMs. In addition to extremely high intensity, the photocathode has the advantage that the interval of electron beam emission is easily controlled by controlling the laser irradiation. For example, a pulsed electron beam can be obtained by irradiation with a pulsed laser. A pulsed electron beam enables us to observe an organism in vivo because it does not cause fatal irradiation damage. We could deposit a Cs₃Sb photocathode on a small selected area of a cathode tip by limiting the area of Sb and Cs deposition using a mask with a small hole [4]. Therefore, another advantage is the ability to easily change the size and shape of the electron beam by changing the shape of the photoemissive coating. In addition, our previous research found that the photocurrent from a Cs₃Sb photocathode increased with increasing anode voltage from 0.4 to 7.0 kV [4].

Despite the many advantages of the photocathode mentioned above, it has not been applied as an electron source for TEMs because many problems remain to be solved. The most important problem with the use of a photocathode coated with a photoemissive material such as Cs₃Sb in TEMs is that the quantity of photoelectrons decreases rapidly with time in a vacuum chamber with an inadequate vacuum level. For a photocathode coated with Cs₃Sb, the decrease in photoelectron emission is thought to be caused by destruction of the crystal structure resulting from oxidation of the Cs₃Sb photocathode and gradual loss of Cs [5]. It is also a serious problem that it is difficult to

transfer the Cs₃Sb photocathode from the vacuum chamber for deposition of Sb and Cs to a TEM without reducing its photoemission. The use of other photoemissive materials poses the same problem because these materials are extremely chemically active. They have been used in evacuated glass tubes such as photodiodes, photomultipliers, and imaging tubes, but they have extremely long lifetimes. The extremely long lifetime of a Cs₃Sb photocathode in an evacuated glass tube, for example, seems to result from the presence of a small amount of residual Cs vapor in the tube, because this residual Cs vapor replaces any Cs that may be lost from the cathode surface and also attracts any oxygen that might poison the cathode [5]. On the other hand, when a Cs₃Sb photocathode is used in a TEM or other vacuum chamber facility, the lifetime is thought to be much shorter than that in an evacuated glass tube. A short lifetime of a Cs₃Sb photocathode in a vacuum chamber has been reported [4, 5], and efforts have also been made recently to increase the lifetimes of Cs₃Sb and K–Cs–Sb photocathodes [6-9].

We found previously that the photocurrent from a Cs₃Sb photocathode decreased with increasing anode voltage from 0.1 to 0.4 kV and increased with increasing anode voltage from 0.4 kV to 7 kV [4]. We did not obtain data about the anode voltage dependence of the photocurrent for voltages below 0.1 kV because the accuracy of the potentiometer was limited. The first objective of the present research is to determine the photocurrent from a Cs₃Sb photocathode as a function of anode voltage for voltages of 0–0.2 kV.

The conventional method of fabricating a Cs₃Sb photocathode is to deposit Sb and Cs alternatively on a cathode plate at approximately 130°C [3,5]. However, this method is not suitable for our specially developed deposition equipment, which allows us to coat Cs₃Sb on a small area of a fine cathode tip, because it is almost impossible for the equipment to switch quickly between deposition of Sb and Cs [4, 10]. Therefore, we developed a new fabrication method called the sandwich method [4]. In this method, we deposit Sb, Cs, and Sb in order on a cathode tip at a temperature below –10°C and then increased the temperature of the cathode tip to 8–16°C. However, the fabrication conditions required to obtain higher quantum efficiency of photoemission using the sandwich method have not been examined. The second objective of the present research is to find the sandwich method fabrication conditions that yield the highest quantum efficiency of photoemission.

We recently found that the photocurrent of a Cs₃Sb photocathode was significantly increased by additional Cs deposition at elevated temperature [10]. Because the quantum efficiency of Cs₃Sb photocathodes decreases with elapsed time, its recovery by additional Cs deposition is very important for the use of Cs₃Sb photocathodes in TEMs.

Because the photocurrent decreased rapidly with elapsed time after additional Cs deposition [4], we have to find the conditions required to decrease this reduction in order to make full use of additional Cs deposition. The third objective of the present research is to identify the best conditions for effective recovery of the photoemission from Cs₃Sb photocathodes by additional Cs deposition.

We also found recently that a WO₃ oxide film resulting from deposition of one- or two-atomic-layer-thick W film on the surface of a Cs₃Sb photocathode reduced the rate at which the photocurrent from a Cs₃Sb photocathode decreased [10]. The Cr₂O₃ oxide film resulting from deposition of 1.5-atomic-layer-thick Cr also extended the lifetime of a Cs₃Sb photocathode [10]. We thought that both WO₃ and Cr₂O₃ films in the passive state extended the lifetime of Cs₃Sb photocathodes by protecting the surface from oxygen attack and gradual loss of Cs from Cs₃Sb. The fourth objective of the present research is to examine in detail the effect of WO₃ and Cr₂O₃ films in the passive state on extension of the lifetime of Cs₃Sb photocathodes.

2. Experimental

We previously developed vacuum deposition equipment for coating Cs₃Sb photocathodes on a small area whose diameter is smaller than the cathode tip diameter of 0.2 mm [4]. To detect photoelectrons during additional Cs deposition, we then modified our original equipment by making a 2-mm-diameter hole in the center of the wedge prism used to reflect the laser inside the Faraday cup. Fig. 1 shows the modified deposition equipment for coating Cs₃Sb photocathode on a small area of a fine cathode tip in a vacuum chamber. As shown in this figure, we could deposit additional Cs on a cathode tip while detecting photoelectrons with the Faraday cup. Because the details of our originally developed vacuum deposition equipment were described in our previous report [4], we provide only a brief description of it here. With the developed equipment, we can deposit Sb, Cs, and so forth on a cathode tip by heating a boat using an electron beam. A Cs₃Sb photocathode can be coated on a small area of the fine cathode tip by limiting the Cs and Sb deposition area using an aperture. After confirming the formation of Cs₃Sb on a cathode tip by detection of photoelectrons using a Faraday cup, we set the cathode unit within a small vessel shield in an Ar gas atmosphere with a cover by using a wobblestick (or a type of 3-D manipulator). We can then transfer it from the vacuum deposition equipment to the specially designed or modified TEM without exposing it to air or oxygen.

Fig. 2 shows photographs of our modified TEM which enables us to introduce a photocathode from the small vessel shield in an Ar gas atmosphere into its electron gun.

Fig. 2(a) shows the TEM in the normal condition, and Fig. 2(b) shows the TEM in the condition under which we introduce a photocathode into the electron gun. We introduce the small vessel including a cathode unit with a Cs_3Sb photocathode from the area labeled “Entrance for Cathode.” Because the cover for operation is filled with Ar gas after the vessel is introduced into the cover, we can remove the cathode unit from the vessel and set it in the electron gun using the glove without exposing it to air or oxygen. After we set the cathode unit in the electron gun, we remove the Ar gas from the cover for operation and lower the electron gun unit using the chain block. As shown in Fig. 2(a), we introduce a laser beam into the vacuum vessel of the TEM using an optical fiber and align the focused laser irradiation area and the cathode tip center using two XYZ-stages for an optical fiber and an endoscope, with a monitor for the endoscope.

We previously developed a new method, the so-called sandwich method fabricating Cs_3Sb photocathodes that was suitable for our developed deposition equipment [4, 10]. Fig. 3 shows a schematic diagram of this method. After baking a Ni cathode tip for 2 h at 200°C , we deposited 8-nm-thick Cr on the surface of the cathode tip, because Sb reacts chemically with Ni [3]. After again baking the cathode tip for 2 h at 200°C , we deposited 8-nm-thick Sb, 93-nm-thick Cr and 4-nm-thick Sb at -18 to -12°C , as shown in Fig. 3(a). After the second Sb deposition, we increased the temperature of the cathode tip from -18 to -12°C to 6 – 40°C to form Cs_3Sb . Details of the evaporation of Sb, Cs, and so on were described in our previous report [4].

Table 1 summarizes the experimental conditions. We performed eight experiments, mainly to examine in detail the surface protection provided by WO_3 and Cr_2O_3 thin films in the passive state on Cs_3Sb photocathodes. In experiments I and II, we examined mainly the effects of a WO_3 film, and we examined those of a Cr_2O_3 film in experiments III–VIII. The deposited thicknesses of the W film were one or three atomic layers, and those of the Cr films were one to three atomic layers. Note that the effect of baking in experiment I was larger than that in the other experiments despite a much shorter baking time because of the slightly higher baking temperature. The upper chamber shown in Fig. 1 was evacuated by a cryopump or turbo molecular pump (TMP) in experiments II, V, and VII, but it was evacuated only by the TMP in I, III, IV, VI, and VIII. In all the experiments, the effects of additional Cs deposition on the photoemission were examined before or during the lifetime test of photoemission from the Cs_3Sb photocathode.

3. Results and Discussion

3.1 Photocurrent as a function of anode voltage below 200 V

In our previous research we extracted photoelectrons from Cs_3Sb using an extracting voltage or anode voltage of 1 kV [4, 10], but in the present research, we extracted photoelectrons using an anode voltage of 0.1 kV.

We previously examined the effect of the anode voltage on the photocurrent from a Cs_3Sb photocathode [4]. We found that the normalized photocurrent decreased from 1.13 to 0.4 with increasing voltage from 0.1 to 0.4 kV, but increased from 0.4 to 1.93 with increasing voltage from 0.4 to 7 kV. Because the photocurrent at 0.1 kV was 1.13 times that at 1 kV, the photocurrent in the present research is almost the same as that in our previous research obtained at 1 kV [4, 10]. As the photocurrent from a Cs_3Sb photocathode as a function of anode voltage has not been reported at anode voltages below 0.1 kV (100 V) [4], we examined precisely the photocurrent at anode voltages below about 200 V in the present research.

Fig. 4 shows the photocurrent as a function of anode voltage below 196 V. The photocurrent was normalized so that it was 1.0 at 9 V. The data were obtained by increasing the anode voltage from 9 to 196 V for 35 min in increments of approximately 10 V. The normalized photocurrent increased gradually from 1.0 to 1.24 with increasing voltage from 9 to 39 V and increased rapidly from 1.24 to 3.27 with increasing voltage from 39 to 68 V. The normalized photocurrent then decreased gradually from 3.27 to 2.57 with increasing voltage from 68 to 196 V. The decrease in photocurrent as the anode voltage increased from 68 to 196 V corresponds well qualitatively to our previous report, in which the normalized photocurrent decreased from 1.130 to 0.724 with increasing voltage from 100 to 200 V [4]. In the present research, the ratio of photocurrent at 98 V to that at 196 V was 0.839. However, in our previous research, the ratio of the photocurrent at 100 V to that at 200 V was 0.641 [4]. This quantitative discrepancy could be caused by the lower accuracy of the voltage in our previous research, because the minimum scale of the voltage in the potentiometer was 10 V in the present research but 200 V in our previous experiment [4].

Fig. 5 shows the photocurrent as a function of anode voltage below 196 V, where the anode voltage was increased extremely slowly. The photocurrent was normalized so that it was 1.0 at 9 V, and the data were obtained by increasing the anode voltage from 3 to 196 V for 61.5 min in increments of approximately 5 V. The normalized photocurrent increased rapidly from 0.00 to 1.76 with increasing voltage from 0 to 14 V, but decreased from 1.76 to 1.24 with increasing voltage from 14 to 19 V. The normalized photocurrent decreased very slowly from 1.33 to 0.810 with increasing voltage from 24 to 93 V, but it increased abruptly from 0.905 to 5.52 from 98 to 102.5 V. The normalized photocurrent then decreased slowly from 5.52 to 4.86 with increasing

anode voltage from 102.5 to 196 V.

The large difference between Figs. 4 and 5 suggests that the photocurrent was significantly affected by the speed at which the anode voltage was increased below 200 V. This phenomenon is physically very interesting, and it might give us important information for understanding photoelectric emission. We do not explain this phenomenon theoretically at present. Because we usually increased the anode voltage from 0 to 100 V within 10 s, the effect of this phenomenon could be ignored in measuring the photocurrent in the present research.

3. 2 Fabrication of Cs_3Sb photocathode with “sandwich method”

We tried to identify better fabrication conditions using the sandwich method that would yield more photoelectrons. The results of experimental fabrication of Cs_3Sb photocathodes are shown in Table 2. We show the quantum efficiency for the first-detected photocurrent, the first detection time t after the second Sb deposition (in parentheses), the cathode temperature change between the second Sb deposition and the first photocurrent detection time t , and the vacuum level at the cathode tip. There have been several reports on the quantum efficiency spectra of semitransparent Cs_3Sb photocathodes fabricated by exposing Cs to Sb deposited on a glass plate at a temperature of 130–150°C in an evacuated glass tube [1, 11, 12]. The quantum efficiencies of the Cs_3Sb photocathodes at 405 nm were 11.1% [1], 6.8% [11], and 18.6% [12]. The quantum efficiencies of the Cs_3Sb photocathodes in experiments II, III, and VI are comparable to these values. As shown in table 2, however, the quantum efficiency varied significantly among the eight experiments.

Fig. 6 shows the temperature of the cathode tips as a function of elapsed time from the second Sb deposition to the first detection of photocurrent in experiments I, IV, V, and VIII, the first-detected quantum efficiencies of which were smaller than 1%. Fig. 7 shows the same graph as Fig. 6 for experiments II, III, IV, and VII, the first-detected quantum efficiencies of which were larger than 1%. In these figures, we show the first-detected quantum efficiencies in each case. When we compare Figs. 6 and 7, large difference between them becomes apparent. The temperature increased in steps in the experiments with quantum efficiencies smaller than 1 % (II, III, IV, and VIII), as shown in Fig. 6, but it increased smoothly in the experiments with quantum efficiencies larger than 1 % (II, III, IV, and VIII), as shown in Fig. 7. This feature implies that a smooth increase in the cathode temperature after the second Sb deposition is necessary for obtaining a higher quantum efficiency.

In experiment IV, the extremely small quantum efficiency of 0.0385% could

be caused partly by the low cathode temperature of 6°C when the photocurrent was first detected, because the cathode temperature increased almost smoothly (Fig. 6). On the other hand, the quantum efficiency of 2.58% in experiment III was not small despite the low cathode temperature of 7°C when the photocurrent was first detected (Fig. 7). The great difference in quantum efficiency between experiments IV and III does not seem to be explained only by the difference in cathode temperature and the smooth increase in cathode temperature. However, the time at which the cathode temperature began to increase after the second Sb deposition and the initial speed of the temperature increase differed significantly between experiments IV and III. In experiment IV, the cathode temperature was -15°C at 0, 1, and 3 min, and -6°C at 8 min. In experiment III, the cathode temperature was -16°C at 0 and 1 min, -12°C at 3 min, -5°C at 6 min, -2°C at 8 min. We expect, therefore, that the difference in the temperature increase, especially from 0 to 3 min, could be the main cause of the large difference in quantum efficiency between experiments IV and III.

This expectation regarding the results of experiments IV and III is roughly consistent with the other results. As shown in Fig. 6, the temperature increase from 0 to 3 min was 5°C in experiment VIII, where the quantum efficiency was 0.510%, and it was 0°C in experiment I, where the quantum efficiency was 0.319 %. We cannot comment on experiment V because we had no data on the cathode temperature at 3 min. As shown in Fig. 7, the temperature increase from 0 to 3 min was 1°C in experiment IV, where the quantum efficiency was 9.17%; 2°C in experiment II, where the quantum efficiency was 4.95%; and 0°C in experiment VII, where the quantum efficiency was 1.06%. The apparent anomaly between experiments II and IV could be explained by two facts. First, the cathode temperature at which the photocurrent was first detected in experiment II was 12°C lower than that in experiment IV. In addition, the secondary cathode temperature at 0 min in experiment II was 6°C lower than that in experiment IV.

3.3 Recovery of photoemission from Cs₃Sb photocathode by additional Cs deposition

We found previously that an additional Cs deposition on a Cs₃Sb photocathode at elevated temperature increased the photoemission of the Cs₃Sb photocathode [10]. In the present research we tried to find the optimal experimental condition for recovery of the photocurrent. Our previous experimental results suggested that the optimal cathode temperature for additional Cs deposition in our evaporation-boat heater would be between approximately 50°C and 80°C [10]. Our previous results also suggested that increasing the cathode temperature during Cs deposition would be favorable for

increasing the photocurrent. In contrast, it was suggested that decreasing the cathode temperature during Cs deposition would not be favorable for increasing the photocurrent.

Table 3 summarizes the results regarding the recovery of photoemission from Cs₃Sb photocathodes by additional Cs deposition. On the left side of this table, we show the quantum efficiency Q_s at the time that additional Cs deposition began, the maximum quantum efficiency $Q_{\max}$ during additional Cs deposition, the ratio $Q_{\max}/Q_s$, the change in cathode temperature during additional Cs deposition, and the period Δt (min) of Cs deposition. On the right side, we show the quantum efficiency Q_t at time t , the time t_e (min) at which photocurrent detection ended after Cs deposition ended (in parentheses), the ratio $Q_t/Q_{\max}$, and the decrease in temperature from $t = 0$ to $t = t_e$. The quantum efficiencies were increased significantly by additional Cs deposition in all the experiments. However, the ratio $Q_{\max}/Q_s$ differed greatly among the experiments. The maximum value was 426.1 in experiment VII, and the minimum value was 2.6 in experiment VIII. Following the suggestion from our previous results, we tried to realize temperatures that were between 50 and 67°C for the Cs₃Sb photocathode and that increased gradually or remained constant during additional Cs deposition, as shown in table 3. From the results shown in table 3, the cathode temperature of 50–70°C during additional Cs deposition is favorable for effectively increasing the photoemission. The ratio $Q_t/Q_{\max}$ is relatively large for experiments II, V, and VII. This means that the reduction in photocurrent after Cs deposition was small in these experiments.

We obtained graphs showing the normalized photocurrent and cathode temperature as a function of the elapsed time during additional Cs deposition for all eight experiments. **Figs. 8–10** show the graphs for experiments I, V, and VII, respectively, as typical examples. In these figures, the photocurrent is normalized to be unity at $t = 0$ min, and the period of additional Cs deposition is indicated by arrows. In most cases, the photocurrent increased with increasing time of additional Cs deposition, and it reached a maximum near the end of Cs deposition.

As shown in **Fig. 8**, the normalized photocurrent increased steeply from 1 to approximately 173 between 25 and 41 min. The cathode temperature was 60–61°C during Cs deposition. After 41 min, the photocurrent increased slowly, and the normalized photocurrent had a maximum of 181.7 at 53 min, which was 8 min before Cs deposition ended. The quantum efficiency corresponding to the maximum photocurrent at 53 min was 2.06%, which is not the maximum value for the Cs₃Sb photocathodes. We think that photocurrent stopped increasing at approximately 45 min because of a decrease in the Cs evaporation rate due to a decrease in the amount of

evaporative material for Cs (CsCrO_4) in the boat. The normalized photocurrent decreased rapidly from 179.8 to 98.4 between 61 and 110 min, as shown in Fig. 8. A rapid decrease in photocurrent after additional Cs deposition was observed in most of the experiments. A rapid decrease in photocurrent with time also occurs just after fabrication of Cs_3Sb photocathodes [4, 10]. As shown in table 3, $Q_t/Q_{\max}$ is relatively large in experiments II, V, and VII. This means that the photocurrent did not decrease rapidly after additional Cs deposition in these experiments. Because $Q_{\max}/Q_s$ was only 2.6 during additional Cs deposition in experiment II, we think that this small increase could be the cause of the small reduction after additional Cs deposition. Therefore, we should examine in detail the results of experiments V and VII to find the cause of the small reduction in photocurrent after additional Cs deposition ended.

As shown in Fig. 9, the normalized photocurrent increased from 1.0 to 13.4 between 35 and 65 min during additional Cs deposition in experiment V. The cathode temperature increased rapidly from 52 to 58°C between 35 and 45 min, but it increased slowly from 58 to 62°C between 45 and 65 min. After Cs deposition, we decreased the cathode temperature rapidly from 61 to 41°C between 65 and 75 min, and then we decreased it gradually from 41 to 39°C between 75 and 110 min. The normalized photocurrent showed a corresponding decrease from 13.4 to 10.4 between 75 and 110 min. The reduction in photocurrent after additional Cs deposition in experiment V was smaller than that in the other experiments except for experiment VII. The fact that the temperature was maintained around 40°C between 75 and 110 min is likely the cause of the smaller reduction in photocurrent after additional Cs deposition in experiment V. This is similar to the result in our previous research [10].

As shown in Fig. 10, the normalized photocurrent increased from 1.0 to 426.1 between 35 and 75 min during additional Cs deposition in experiment VII. The cathode temperature increased very slowly from 63 to 67°C between 35 and 75 min. Because the increase in photocurrent after additional Cs deposition was very large in experiment VII, keeping the temperature around 65°C would be preferable during additional Cs deposition. After Cs deposition, we decreased the cathode temperature gradually from 67 to 44°C between 75 and 110 min, and the normalized photocurrent showed a corresponding gradual decrease from 426.1 to 383.5. The rate at which the photocurrent decreased after Cs deposition was slowest in experiment VII. We think that the gradual decrease in photocurrent after additional Cs deposition in experiment VII was caused by the gradual decrease in cathode temperature.

In summary, additional Cs deposition resulted in significant recovery of the photocurrent from a Cs_3Sb photocathode if the cathode temperature was maintained

between approximately 50°C and approximately 70°C under the present experimental conditions. The rapid reduction in photocurrent after additional Cs deposition was suppressed most effectively by gradually decreasing the cathode temperature to approximately 40–45°C. Therefore, we think that the installation of a device for evacuation of Cs within TEMs would be very helpful to realize the use of Cs₃Sb photocathodes for TEMs, because we could recover the photoemission from the cathodes almost perfectly by using the evaporation device at intervals. Because a sufficiently high vacuum level should be maintained in the chamber containing the Cs₃Sb photocathode, we should remove the evaporation device from the chamber after evaporation without decreasing vacuum level of the TEM chamber at all and isolate it from the TEM chamber using an isolation valve.

3.4 Surface protection of Cs₃Sb photocathode by WO₃ or Cr₂O₃ film in passive state

We performed lifetime tests in the eight independent experiments listed in table 1 (I–VIII), and we examined the surface protection effects of WO₃ or Cr₂O₃ during these tests. We obtained eight graphs showing the common logarithm of the normalized photocurrent as a function of elapsed time for each experiment. We show the graphs for experiments II and VIII as typical examples in order to explain in detail the effects of WO₃ or Cr₂O₃.

Figs. 11 and 12 show the common logarithm of the normalized photocurrent as a function of the elapsed time in experiment II, in which we examined the surface protection effect of WO₃ in the passive state. Fig. 11 shows the result between 0 and 190 h, and Fig. 12 shows that between 190 and 357 h. We found previously that the common logarithm of the photocurrent decreased linearly under the same physical conditions [4, 10], so we used the common logarithmic scale instead of the linear scale in these graphs. As shown in table 1, we performed additional Cs deposition 18 h before the lifetime test began. During the lifetime test, the photocurrent was measured after approximately 10 s of laser irradiation. As shown in Fig. 11, we deposited three atomic layers (a total of 0.95 nm in thickness) of W at $t = 8\text{--}9$ h during the lifetime test in experiment II. Before W deposition, the common logarithm of the photocurrent decreased at a rate of approximately $-0.00842/\text{h}$ starting at 0 h, but it decreased rapidly at a rate of approximately $-0.679/\text{h}$ during W deposition. Deposition of the W film decreased the photocurrent by a factor of approximately 0.41. It took approximately 63 min to deposit three atomic layers (a total of 0.95 nm in thickness) of W, and the vacuum level during deposition of the W film was reduced to $1.8\text{--}3.0 \times 10^{-7}$ Pa. This reduction in vacuum level could be the main cause of the rapid decrease in photocurrent during W deposition.

Another cause could be absorption of photoelectrons by the W film. After deposition of the W film, the common logarithm of the photocurrent decreased gradually at a rate of approximately $-0.00162/\text{h}$ until 124 h. We think that WO_3 was formed during the period of 63 min during which the W film was deposited because the vacuum level was low enough for the W film to be oxidized. We think that the WO_3 in the passive state that formed during deposition of the W film caused this extremely slow decrease in the common logarithm of the photocurrent from 9 to 124 h by protecting the surface of the Cs_3Sb photocathode.

We irradiated the cathode tip continuously with a 405 nm laser between 125 and 245 h. The laser intensity at the surface of the cathode tip was $0.0016 \text{ W}/\text{cm}^2$ from 125 to 149 h and $0.0017 \text{ W}/\text{cm}^2$ from 149 to 245 h (Figs. 11 and 12). Note that we extracted photoelectrons continuously from 145 to 179 h. The common logarithm of the photocurrent decreased at a rate of $-0.00958/\text{h}$ between 125 and 149 h, at a rate of $-0.00901/\text{h}$ between 149 and 179 h, and at a rate of $-0.00452/\text{h}$ between 179 and 245 h. Therefore, the rate at which the photocurrent decreased was enhanced by continuous laser irradiation. An enhanced rate of decrease under continuous laser irradiation was also observed in our previous research [10]. We think that this phenomenon could be caused by photo-oxidation. Light irradiation is known to promote chemical reactions in a material because absorption of light increases the energy of electrons in the material. If oxidation of the Cs_3Sb photocathode is enhanced by laser irradiation, the quantum efficiency of the photocathode could decrease more rapidly because oxidation poisons the photocathode. We think that the rate between 179 and 245 h, $-0.00452/\text{h}$, was somewhat smaller than that between 125 and 149 h, $-0.00958/\text{h}$, because the WO_3 was strengthened by photo-oxidation during continuous laser irradiation.

When we reduced the vacuum level from 1.1×10^{-7} to $2.1 \times 10^{-7} \text{ Pa}$ at 245 h, the common logarithm of the photocurrent decreased rapidly at a rate of $-0.309/\text{h}$ between 245 and 246 h. However, the common logarithm of the photocurrent decreased very slowly (at a rate of $-0.00177/\text{h}$) between 250 and 271 h. The vacuum level was changed by changing the evacuation pump for the upper chamber from the cryopump to the TMP. We think that the much slower decrease between 250 and 271 h was caused by re-strengthening of the WO_3 in the passive state due to oxidization during the period of lower vacuum level between 245 and 246 h, which provided better protection for the surface of the Cs_3Sb photocathode. We gradually increased the temperature of the upper chamber containing the cathode tip between 269 and 275 h from 6 to 26°C . In conjunction with this temperature increase, the common logarithm of the photocurrent decreased somewhat more steeply, at a rate of $-0.0198/\text{h}$, between 271 and 275 h. We

think that the increase in the temperature of the upper chamber from 6 to 26°C caused the more rapid decrease in the photocurrent by increasing the vapor pressure of H₂O in the upper chamber, which enhanced the oxidation of the Cs₃Sb photocathode. The common logarithm of the photocurrent decreased very slowly (at a rate of -0.00352/h) between 275 and 293 h.

We again applied continuous laser irradiation beginning at 293 h. The common logarithm of the photocurrent decreased rapidly (at a rate of -0.103/h) between 293 and 295 h, but it became almost constant between 295 and 297 h, probably because of re-strengthening of WO₃ in the passive state by photo-oxidation. We changed the vacuum level from 2.1×10^{-7} to 1.1×10^{-7} Pa at 297 h; the common logarithm of the photocurrent then increased at a rate of +0.00352/h between 297 and 313 h. After we increased the laser intensity from 0.0016 to 0.0037 W/cm² at 313 h, the common logarithm of the photocurrent decreased at a rate of -0.0506/h until 314 h, and it decreased at a rate of -0.00454/h between 314 and 336 h. After we reduced the vacuum level from 1.1×10^{-7} to 2.1×10^{-7} Pa at 336 h, the common logarithm of the photocurrent decreased at a rate of -0.0221/h between 336 and 343 h under a laser intensity of 0.0016 W/cm². It decreased at a rate of -0.0377/h between 343 and 357 h under a laser intensity of 0.0037 W/cm².

The analysis of Figs. 11 and 12 indicated that deposition of the three-atomic-layer (0.95-nm-thick) W film greatly extended the lifetime of the photoemission of the Cs₃Sb photocathode after the W film was oxidized to WO₃ in the passive state. The WO₃ could provide more protection for the Cs₃Sb photocathode surface after the vacuum level was reduced. The protective effect of WO₃ could also be strengthened by photo-oxidation during continuous laser irradiation.

Figs. 13 and 14 show the common logarithm of the normalized photocurrent as a function of the elapsed time in experiment VII, in which we examined the surface protection effect of Cr₂O₃ in the passive state. Fig. 13 shows the result between 0 and 250 h, and Fig. 14 shows that between 250 and 455 h. After the common logarithm of the normalized photocurrent decreased rapidly between 0 and 5 h, it decreased at a rate of -0.0149/h between 5 and 23 h. We deposited three atomic layers (a total of 0.87 nm in thickness) of Cr at approximately 23.5 h. As shown in Fig. 13, deposition of the Cr film decreased the photocurrent by a factor of approximately 0.34. It took approximately 5 min to deposit three atomic layers of Cr, and the vacuum level during deposition of the Cr film was reduced to $1.6\text{--}2.1 \times 10^{-7}$ Pa. We think that both the reduction of the vacuum level during deposition of the Cr film and the absorption of photoelectrons by the Cr film were the main causes for the rapid decrease in

photocurrent during Cr deposition. The common logarithm of the photocurrent decreased gradually at a rate of approximately $-0.00795/\text{h}$ between 29 and 42 h. We think that the Cr_2O_3 in the passive state, which was not so strong to protect the surface of the Cs_3Sb photocathode, was formed during the period of 5 minutes for the deposition of Cr film because the vacuum level was low for the Cr film to be oxidized. After we reduced the vacuum level from 1.1×10^{-7} to 2.2×10^{-7} Pa at 42 h, the common logarithm of the photocurrent decreased rapidly (at a rate of $-0.306/\text{h}$) between 42 and 45 h.

After this rapid decrease in the common logarithm of the photocurrent, the rate of decrease became increasingly smaller. The common logarithm of the photocurrent decreased very slowly (at a rate of $-0.00152/\text{h}$) between 186 and 214 h. We think that the surface protection by Cr_2O_3 in the passive state was strengthened during the long period from 42 to 186 h. The rate of decrease, $-0.00152/\text{h}$, for Cr_2O_3 was smaller than that between 275 and 293 h for WO_3 , $-0.00352/\text{h}$. This result suggests that the maximum surface protection provided by Cr_2O_3 in the passive state formed from three atomic layers of Cr could be stronger than that provided by WO_3 in the passive state formed from three atomic layers of W.

We changed the vacuum level from 2.2×10^{-7} to 1.0×10^{-7} Pa at 211 h, and we deposited additional Cs between 214 and 215 h. The photocurrent increased by 426.1 times after this additional Cs deposition. This is the first observation of effective recovery of the photoemission of a Cs_3Sb photocathode by additional Cs deposition even when the cathode's surface was coated with Cr_2O_3 in the passive state. This could imply that Cs atoms penetrated the protective Cr_2O_3 in the passive state. The common logarithm of the photocurrent decreased at a rate of $-0.00740/\text{h}$ between 216 and 238 h. Because the rate of $-0.00740/\text{h}$ was larger than that between 186 and 211 h, $-0.00152/\text{h}$, when the vacuum level was 2.2×10^{-7} Pa, we think that the surface protection by Cr_2O_3 in the passive state was seriously weakened by additional Cs deposition. As shown in Figs. 13 and 14, the rate of decrease of the common logarithm of the photocurrent became slow between 216 and 309 h. It decreased at a rate of $-0.00163/\text{h}$ between 282 and 309 h.

We again reduced the vacuum level from 1.0×10^{-7} to 2.0×10^{-7} Pa at 309 h. The common logarithm of the photocurrent decreased rapidly (at a rate of $-0.155/\text{h}$) between 309 and 314 h. This result clearly confirmed that the surface protection effect of Cr_2O_3 in the passive state was almost eliminated by additional Cs deposition, because the rate of $-0.155/\text{h}$ was almost equivalent to that between 42 and 45 h, $-0.306/\text{h}$. This implies that the crystal structure of Cr_2O_3 in the passive state was completely destroyed

by additional Cs deposition. After the common logarithm of the photocurrent decreased rapidly between 307 and 314 h, it very quickly became almost zero. The common logarithm of the photocurrent decreased at a rate of $-0.000832/\text{h}$ between 316 and 356 h. This implies that Cr_2O_3 in the passive state was formed again within a very short time. Because the rate of $-0.000832/\text{h}$ is much smaller than that between 186 and 211 h, $-0.00152/\text{h}$, the Cr_2O_3 in the passive state that re-formed between 309 and 316 h was much stronger than that which was formed first between 42 and 186 h. We changed the vacuum level from 2.0×10^{-7} to 1.0×10^{-7} Pa at 356 h. The common logarithm of the photocurrent then increased at a rate of $+0.00305/\text{h}$ between 356 and 378 h. An increase in the photocurrent from a Cs_3Sb photocathode has not been reported to date. This phenomenon is extraordinary and is not yet understood.

We applied continuous irradiation by a 405 nm laser between 378 and 430 h. The common logarithm of the photocurrent decreased rapidly (at a rate of $-0.184/\text{h}$) between 378 and 378.5 h, but the rate decreased gradually after 378.5 h. The common logarithm of the photocurrent decreased more slowly (at a rate of $-0.0192/\text{h}$) between 383 and 385 h. As shown in Fig. 14, we increased the laser intensity at the cathode tip from 0.16 to 0.52 W/cm^2 at 385 h. The common logarithm of the photocurrent then decreased rapidly (at a rate of $-0.0859/\text{h}$) between 385 and 386 h, but it decreased more slowly after 386 h. The common logarithm of the photocurrent decreased at a rate of $-0.00530/\text{h}$ between 402 and 405 h. At 405 h, we reduced the vacuum level from 1.0×10^{-7} to 2.0×10^{-7} Pa and changed the laser intensity at the cathode tip from 0.52 to 0.15 W/cm^2 . Then the common logarithm of the photocurrent decreased rapidly (at a rate of $-0.116/\text{h}$) between 405 and 406 h, and it decreased at a rate of $-0.0493/\text{h}$ between 407 and 409 h. We increased the laser intensity at the cathode tip from 0.15 to 0.53 W/cm^2 at 409 h. The common logarithm of the photocurrent then decreased at a rate of $-0.0647/\text{h}$ between 409 and 411 h, but the rate decreased gradually after 411 h. The common logarithm of the photocurrent decreased at a rate of $-0.0172/\text{h}$ between 425 and 428 h.

We further reduced the vacuum level from 2.0×10^{-7} to 3.9×10^{-7} Pa and stopped the continuous laser irradiation at 428 h. The common logarithm of the photocurrent then decreased rapidly (at a rate of $-0.0814/\text{h}$) between 428 and 430 h. However, the rate decreased at 430 h, and it was $-0.0224/\text{h}$ between 430 and 450 h. The common logarithm of the photocurrent decreased rapidly (at a rate of $-0.0923/\text{h}$) between 450 and 453 h. We think that the rate of decrease between 430 and 450 h was smaller than those in the preceding and following periods because we did not measure the photocurrent between 430 and 450 h. We again started continuous laser irradiation at

a laser intensity of 0.18 W/cm^2 at the cathode tip at 453 h. The common logarithm of the photocurrent then decreased very rapidly (at a rate of 0.286/h) between 453 and 454 h.

Table 4 summarizes the experimental results regarding the effects of surface protection of the Cs_3Sb photocathode by WO_3 or Cr_2O_3 in the passive state. For each experiment, we show the vacuum level, laser irradiation condition, rate at which the common logarithm of the photocurrent decreased before and after formation of WO_3 or Cr_2O_3 , and temperature of the chamber. We compare the rate at which the common logarithm of the photocurrent decreased before and after formation of WO_3 or Cr_2O_3 in the passive state. In this table, G_A/G_B is the ratio of the rate of decrease of the common logarithm of the photocurrent after formation of WO_3 or Cr_2O_3 in the passive state to that before its formation. Therefore, G_A/G_B is an index of the strength of the surface protection of the Cs_3Sb photocathode by WO_3 or Cr_2O_3 in the passive state. If G_A/G_B is small, the effect of surface protection by WO_3 or Cr_2O_3 in the passive state is large.

As shown in table 4, G_A/G_B was 0.605 for the WO_3 in the passive state formed from the one-atomic-layer W film in experiment I, and it was 0.0114 for the WO_3 in the passive state formed from the three-atomic-layer W film in experiment II. Both ratios were taken under intermittent laser irradiation. Therefore, the WO_3 in the passive state formed from the three-atomic-layer W film in experiment II protected the surface of the Cs_3Sb photocathode much more effectively than that formed from the one-atomic-layer W film in experiment I. This result is quite reasonable because the thicker oxide film in the passive state could protect the surface of the Cs_3Sb photocathode more effectively. If the absorption of photoelectrons by WO_3 in the passive state is negligible, the effectiveness of surface protection by WO_3 in the passive state increases with increasing WO_3 thickness.

For intermittent laser irradiation, the G_A/G_B value of the Cr_2O_3 in the passive state formed from the one-atomic-layer Cr film in experiment III was 0.187, that of the film formed from the one-atomic-layer Cr film in experiment IV was 0.739, that of the film formed from the two-atomic-layer Cr film in experiment VI was 0.479, and that of the film formed from the three-atomic-layer Cr film in experiment VII was 0.000832. For continuous laser irradiation, the G_A/G_B value of the Cr_2O_3 in the passive state formed from the 1.5-atomic-layer Cr film in experiment V was 0.181, and that of the film formed from the three-atomic-layer Cr film in experiment VIII was 0.0528. These results imply that thicker Cr_2O_3 in the passive state protects the surface of the Cs_3Sb photocathode more effectively. This tendency is the same as that for WO_3 in the passive state. If the absorption of photoelectrons by Cr_2O_3 in the passive state is negligible, therefore, the effectiveness of surface protection by Cr_2O_3 in the passive state increases

with increasing Cr_2O_3 thickness. The difference in G_A/G_B between experiments III and IV was caused by the difference in the rate G_B between them. As shown in table 4, the temperature of the upper chamber was 27°C in experiment III, but it was $7\text{--}26^\circ\text{C}$ in experiment IV. We think the difference in the temperature of the upper chamber caused the difference in G_B between the experiments because the higher temperature produced more H_2O vapor, which enhanced oxidization of the Cs_3Sb photocathode. When we took the data for G_A , on the other hand, the temperature of the upper chamber was approximately 27°C in both experiments. This is consistent with the result that G_A was almost the same in the two experiments, as shown in table 4.

When we compare the effectiveness of surface protection of the Cs_3Sb photocathode by WO_3 in the passive state and by Cr_2O_3 in the passive state, we should adopt the ratio $G_A/G_B = 0.187$ from experiment III as the ratio for the one-atomic-layer Cr film, for the reason given above. Therefore, as shown in table 4, the Cr_2O_3 in the passive state formed from the one-atomic-layer Cr film protected the surface of the Cs_3Sb photocathode more effectively than the WO_3 formed from the one-atomic-layer W film. Because the G_A/G_B value of 0.00382 in experiment VII was smaller than that in experiment II, 0.0114, the Cr_2O_3 in the passive state formed from the three-atomic-layer Cr film protected the surface more effectively than the WO_3 from the three-atomic-layer W film. Therefore, we conclude that Cr_2O_3 in the passive state protects the surface of the Cs_3Sb photocathode more effectively than WO_3 in the passive state, if these oxide films are formed from films having the same number of atomic layers.

Because the protection of the surface of the Cs_3Sb photocathode by Cr_2O_3 in the passive state was not sufficient for use of the cathode at the vacuum level in typical TEMs, we abandoned the use of the cathode tip coated with the Cs_3Sb photocathode in the modified TEM shown in Fig. 2. However, we found that Cr_2O_3 in the passive state provides stronger surface protection as its thickness increases. We hope that in future the protective effect of Cr_2O_3 in the passive state formed from a Cr film that is reasonably thick will be sufficient for use at the vacuum level of TEMs.

4. Conclusions

We examined 1) the photocurrent as a function of anode voltage below 200 V, 2) the relationship between the quantum efficiency and the conditions under which Cs_3Sb photocathodes were fabricated by the so-called sandwich method, 3) recovery of the photoemission of Cs_3Sb photocathodes by additional Cs deposition, and 4) the protective effect of WO_3 and Cr_2O_3 in the passive state on the surface of Cs_3Sb

photocathodes.

We found that the photocurrent was significantly affected by the rate of increase of the anode voltage used to extract photoelectrons. When we increased it at a typical speed, the photocurrent increased with increasing voltage from 0 to 68 V, but it decreased gradually from 68 to 196 V. When we increased it very slowly, however, the photocurrent decreased gradually with increasing voltage from 24 to 93 V, but it increased steeply when the voltage was around 98 V.

We found that three conditions are necessary to fabricate Cs₃Sb photocathodes with higher quantum efficiency using the sandwich method. First, we have to increase the cathode temperature smoothly after the second Sb deposition at low temperature. Second, we have to start increasing the cathode temperature as soon as possible after the second Sb deposition. Third, we have to increase the cathode temperature to 25–40°C after the second Sb deposition.

We also identified the conditions for effective recovery of photoemission from Cs₃Sb photocathodes by additional Cs deposition. First, we have to deposit Cs at a cathode temperature of 50–70°C to effectively increase the photoemission. Second, we have to gradually decrease the cathode temperature to within 40–45°C to minimize the reduction in photocurrent after additional Cs deposition. We think that installation of a device for evacuation of Cs within a TEM would be very helpful to realize the use of Cs₃Sb photocathodes in TEMs.

We examined in detail the effect of surface protection of the Cs₃Sb photocathode by WO₃ or Cr₂O₃ in the passive state during lifetime tests in eight experiments. We found that deposition of a 1- or 3-atomic-layer W film and of a 1-, 1.5-, 2-, or 3-atomic-layer Cr film greatly extended the lifetime of photoemission from the Cs₃Sb photocathode after the W or Cr film was oxidized to WO₃ or Cr₂O₃ in the passive state. The protective effect of WO₃ or Cr₂O₃ in the passive state on the surface of the Cs₃Sb photocathode became stronger after both further oxidation under lower vacuum and photo-oxidation during continuous laser irradiation. We concluded that the effect of surface protection by a WO₃ or Cr₂O₃ film in the passive state increases with increasing film thickness. We also concluded that Cr₂O₃ in the passive state protects the surface of the Cs₃Sb photocathode more effectively than WO₃ in the passive state, if these oxide films are formed from films having the same number of atomic layers.

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Figure Captions

Fig. 1 Developed vacuum deposition device for fabricating Cs₃Sb photocathode on a small area of a fine cathode tip under high vacuum.

Fig. 2 Modified TEM, which enables us to introduce a photocathode into its electron gun from the enclosed capsule in Ar gas atmosphere.

Fig. 3 Schematic diagram of fabrication of Cs₃Sb on a cathode tip and coating of W or Cr thin film on the surface of Cs₃Sb. (a) Successive deposition of Cr, Sb, Cs, and Sb,

and their planned thicknesses. (b) Formation of Cs₃Sb by increasing the cathode temperature from -16 to -12°C to 6 – 40°C . (c) Deposition of W or Cr thin film to protect Cs₃Sb during the lifetime test.

Fig. 4 Normalized photocurrent as a function of anode voltage below 196 V, which was obtained at elapsed time of 82 h in the lifetime test in experiment II. Data were obtained by increasing the voltage from 9 to 196 V for 35 min in increments of about 10 V.

Fig. 5 Normalized photocurrent as a function of anode voltage below 196 V, which was obtained at elapsed time of 175 h in the lifetime test in experiment II. Data were obtained by increasing the voltage very gradually from 3 to 196 V for 61.5 min in increments of approximately 5 V.

Fig. 6 Temperature of the cathode tip as a function of elapsed time (min) from the second Sb deposition to the first detection of photoelectrons in experiments I, IV, V, and VIII, where the first detected quantum efficiencies were initially smaller than 1%.

Fig. 7 Temperature of the cathode tip as a function of elapsed time (min) from the second Sb deposition to the first detection of photoelectrons for experiments II, III, VI, and VII, where the first detected quantum efficiencies were larger than 1%.

Fig. 8 Normalized photocurrent and cathode temperature as a function of elapsed time during additional Cs deposition in experiment I. The time 0 min corresponds to the elapsed time of 46 h in the lifetime test, and the vacuum level during additional deposition of Cs was 1.6 – 2.5×10^{-7} Pa.

Fig. 9 Normalized photocurrent and cathode temperature as a function of elapsed time during additional Cs deposition in experiment V. The time 0 min corresponds to 1 h before the lifetime test began, and the vacuum level during additional deposition of Cs was 1.6 – 2.0×10^{-7} Pa.

Fig. 10 Normalized photocurrent and cathode temperature as a function of elapsed time during additional Cs deposition in experiment VII. The time 0 min corresponds to the elapsed time of 23 h in the lifetime test, and the vacuum level during additional deposition of Cs was 1.0 – 1.1×10^{-7} Pa.

Fig. 11 Common logarithm of normalized photocurrent as a function of elapsed time from 0 to 190 h in lifetime test of Cs₃Sb photocathode in experiment II. The intensity of the 405 nm laser at the cathode tip during continuous laser irradiation and continuous electron emission, the vacuum level, and the time of W deposition are shown.

Fig. 12 Common logarithm of normalized photocurrent as a function of elapsed time from 190 to 347 h in lifetime test of Cs₃Sb photocathode in experiment II. The intensity of the 405 nm laser at the cathode tip during continuous laser irradiation, and the vacuum level are shown. This figure continues Fig. 11.

Fig. 13 Common logarithm of normalized photocurrent as a function of elapsed time from 0 to 250 h in lifetime test of Cs₃Sb photocathode in experiment VII. The vacuum level, and the times of additional Cs deposition and Cr deposition are shown.

Fig. 14 Common logarithm of normalized photocurrent as a function of elapsed time from 250 to 455 h in lifetime test of Cs₃Sb photocathode in experiment VII. The intensities of the 405-nm laser at the cathode tip during the continuous laser irradiation, and the vacuum level are also shown. This figure continues Fig. 13.

Table 1 Summarization of experimental conditions.

Experiment Number	Deposited film	Baking before Cs ₃ Sb formation			Photoemission lifetime test			
		-----			-----			
		Period (h)	Temperature (°C)	Period (h)	Additional Cs deposition time t_{Cs}	W or Cr deposition time t_W or t_{Cr}	Vacuum level (Pa)	Vacuum pump
I	W: 1 at. layer	48	121 – 142	219	$t_{Cs} = 46$ h	$t_W = 120$ h	$1.2 - 2.2 \times 10^{-7}$	TMP
II (Fig.4&5)	W: 3 at. layer	664	101 – 118	357	$t_{Cs} = -18$ h	$t_W = 9$ h	$1.0 - 2.1 \times 10^{-7}$	Cryo + TMP
III	Cr: 1 at. layer	500	101 – 113	221	$t_{Cs} = 144$ h	$t_{Cr} = 164$ h	$1.8 - 3.0 \times 10^{-7}$	TMP
IV	Cr: 1 at. layer	546	103 – 114	217	$t_{Cs} = -1$ h	$t_{Cr} = 162$ h	$1.8 - 3.4 \times 10^{-7}$	TMP
V	Cr: 1.5 at. layer	670	102 – 109	240	$t_{Cs} = -1$ h	$t_{Cr} = 2$ h	$1.2 - 2.0 \times 10^{-7}$	Cryo + TMP
VI	Cr: 2 at. layer	214	109 – 119	383	$t_{Cs} = 140$ h	$t_{Cr} = 164$ h	$1.8 - 3.5 \times 10^{-7}$	TMP
VII	Cr: 3 at. layer	188	105 – 115	455	$t_{Cs} = 215$ h	$t_{Cr} = 23$ h	$1.1 - 3.9 \times 10^{-7}$	Cryo + TMP
VIII	Cr: 3 at. layer	1940	116 – 123	218	$t_{Cs} = 23$ h	$t_{Cr} = 142$ h	$1.4 - 3.1 \times 10^{-7}$	TMP

Table 2 Summarized results about fabrication of Cs₃Sb by the sandwich method.

Experiment Number	Deposited Film	Quantum efficiency (%) (<i>t</i> min after 2 nd Sb addition)	Cathode temperature change from 2 nd Sb addition to photocurrent detection	Vacuum level at cathode tip (Pa)
I	W: 1 at. layer	0.319 (<i>t</i> = 53)	−12°C → 40°C	1.2×10^{-7}
II	W: 3 at. layer	4.95 (<i>t</i> = 21)	−18°C → 25°C	1.2×10^{-7}
III	Cr: 1 at. layer	2.58 (<i>t</i> = 33)	−16°C → 7°C	1.8×10^{-7}
VI	Cr: 1 at. layer	0.0385 (<i>t</i> = 38)	−15°C → 6°C	1.8×10^{-7}
V	Cr: 1.5 at. layer	0.452 (<i>t</i> = 45)	−16°C → 29°C	1.3×10^{-7}
VI	Cr: 2 at. layer	9.17 (<i>t</i> = 53)	−12°C → 37°C	1.7×10^{-7}
VII	Cr: 3 at. layer	1.06 (<i>t</i> = 53)	−12°C → 37°C	1.2×10^{-7}
VIII	Cr: 3 at. layer	0.510 (<i>t</i> = 53)	−15°C → 35°C	1.3×10^{-7}

Table 3 Summarized results regarding the recovery of photoemission from Cs₃Sb photocathodes by additional Cs deposition.

Experiment	During additional Cs deposition					After additional Cs deposition										
Number	-----					-----										
	Quantum efficiency			Temperature	Period	Quantum efficiency		Ratio	Decrease of Temperature							
	-----			during	Δ (min.)	at time t_e (min.)			-----							
	Start	→Maximum	Ratio	Cs deposition		after Cs deposition			at time t (min.) after Cs deposition							
	$Q_s(\%)$	$Q_{\max}(\%)$	$(Q_{\max}/Q_s)$			$Q_t(\%)$	$(Q_t/Q_{\max})$	$t=0$	$\rightarrow$	$t=5$	$\rightarrow$	$t=10$	$\rightarrow$	$t=20$	$\rightarrow$	$t=t_e$
I (Fig. 8)	0.0113	$\rightarrow$ 2.06	182.3	60°C→61°C	45	1.13	($t_e=49$)	0.549	61°C→	61°C	$\rightarrow$	61°C	$\rightarrow$	56°C	$\rightarrow$	50°C
II	1.57	$\rightarrow$ 4.08	2.6	59°C→58°C	45	3.89	($t_e=30$)	0.953	58°C→53°C	$\rightarrow$	48°C	$\rightarrow$	46°C	$\rightarrow$	45°C	
III	0.000828	$\rightarrow$ 0.106	128.0	68°C→67°C	55	0.0465	($t_e=30$)	0.439	67°C→67°C	$\rightarrow$	61°C	$\rightarrow$	54°C	$\rightarrow$	50°C	
VI	0.0115	$\rightarrow$ 0.881	76.6	63°C→67°C	40	0.397	($t_e=35$)	0.445	67°C	$\rightarrow$	61°C→	54°C	$\rightarrow$	47°C	$\rightarrow$	40°C
V (Fig. 9)	0.367	$\rightarrow$ 4.92	13.4	50°C→61°C	30	3.71	($t_e=45$)	0.780	61°C→44°C	$\rightarrow$	41°C	$\rightarrow$	41°C	$\rightarrow$	40°C	
VI	0.00335	$\rightarrow$ 0.296	88.4	56°C→66°C	45	0.201	($t_e=30$)	0.679	66°C→58°C	$\rightarrow$	52°C	$\rightarrow$	47°C	$\rightarrow$	46°C	
VII (Fig. 10)	0.00111	$\rightarrow$ 0.473	426.1	63°C→67°C	40	0.424	($t_e=35$)	0.896	67°C→65°C	$\rightarrow$	62°C	$\rightarrow$	55°C	$\rightarrow$	44°C	
VIII	0.0675	$\rightarrow$ 1.68	24.9	54°C→65°C	55	1.08	($t_e=30$)	0.643	65°C→54°C	$\rightarrow$	48°C	$\rightarrow$	44°C→	43°C		

Table 4 Summarization of the experimental results regarding the effects of surface protection of the Cs₃Sb photocathode by WO₃ or CrO₃ in the passive state. “Cryo” means a cryopump.

Experiment Number	Deposited film	Experimental conditions and corresponding results during life time test					
		Vacuum (Pa) [Pumping]	Condition of laser irradiation	Rate with which common logarithm of the photocurrent decreased before and after formation of WO ₃ or Cr ₂ O ₃ , and [chamber temperature]			
				Before (G_B) [Temp.]	→	After(G_A) [Temp.]	Ratio (G_A/ G_B)
I	W: 1 at. layer	1.2×10^{-7} [Cryo]	Intermittent	0.00671 /h [6-7°C]	→	0.00406 /h [7°C]	0.605
II (Fig.11&12)	W: 3 at. layer	2.0×10^{-7} [TMP]	Intermittent	0.309 /h [25°C]	→	0.00353 /h [25°C]	0.0114
III	Cr: 1 at. layer	1.8×10^{-7} [TMP]	Intermittent	0.0852 /h [27°C]	→	0.0159 /h [27°C]	0.187
VI	Cr: 1 at. layer	1.9×10^{-7} [TMP]	Intermittent	0.0207 /h [7-26°C]	→	0.0153 /h [27°C]	0.739
V	Cr: 1.5 at. layer	1.0×10^{-7} [Cryo]	Continuous (0.00366W/cm ²)	0.0341 /h [7°C]	→	0.00618 /h [7°C]	0.181
VI	Cr: 2 at. layer	1.6×10^{-7} [TMP]	Intermittent	0.0145 /h [7°C]	→	0.00695 /h [28°C]	0.479
VII(Fig.13&14)	Cr: 3 at. layer	2.0×10^{-7} [TMP]	Intermittent	0.218 /h [5°C]	→	0.000832 /h [5°C]	0.00382
VIII	Cr: 3 at. layer	1.5×10^{-7} [TMP]	Continuous (0.0127W/cm ²)	0.184 /h [7°C]	→	0.00972 /h [7°C]	0.0528

Fig. 1 Developed vacuum deposition device for fabricating Cs_3Sb photocathode on a small area of a fine cathode tip under high vacuum.

Fig. 2 Modified TEM, which enables us to introduce a photocathode into its electron gun from the enclosed capsule in Ar gas atmosphere.

Fig. 3 Schematic diagram of fabrication of Cs_3Sb on a cathode tip and coating of W or Cr thin film on the surface of Cs_3Sb . (a) Successive deposition of Cr, Sb, Cs, and Sb, and their planned thicknesses. (b) Formation of Cs_3Sb by increasing the cathode temperature from -16 to -12°C to $6\text{--}40^{\circ}\text{C}$. (c) Deposition of W or Cr thin film to protect Cs_3Sb during the lifetime test.

Fig. 4 Normalized photocurrent as a function of anode voltage below 196 V, which was obtained at elapsed time of 82 h in the lifetime test in experiment II. Data were obtained by increasing the voltage from 9 to 196 V for 35 min in increments of about 10 V.

Fig. 5 Normalized photocurrent as a function of anode voltage below 196 V, which was obtained at elapsed time of 175 h in the lifetime test in experiment II. Data were obtained by increasing the voltage very gradually from 3 to 196 V for 61.5 min in increments of approximately 5 V.

Fig. 6 Temperature of the cathode tip as a function of elapsed time (min) from the second Sb deposition to the first detection of photoelectrons in experiments I, IV, V, and VIII, where the first detected quantum efficiencies were initially smaller than 1%.

Fig. 7 Temperature of the cathode tip as a function of elapsed time (min) from the second Sb deposition to the first detection of photoelectrons for experiments II, III, VI, and VII, where the first detected quantum efficiencies were larger than 1%.

Fig. 8 Normalized photocurrent and cathode temperature as a function of elapsed time during additional Cs deposition in experiment I. The time 0 min corresponds to the elapsed time of 46 h in the lifetime test, and the vacuum level during additional deposition of Cs was $1.6\text{--}2.5 \times 10^{-7}$ Pa.

Fig. 9 Normalized photocurrent and cathode temperature as a function of elapsed time during additional Cs deposition in experiment V. The time 0 min corresponds to 1 h before the lifetime test began, and the vacuum level during additional deposition of Cs was $1.6\text{--}2.0 \times 10^{-7}$ Pa.

Fig. 10 Normalized photocurrent and cathode temperature as a function of elapsed time during additional Cs deposition in experiment VII. The time 0 min corresponds to the elapsed time of 23 h in the lifetime test, and the vacuum level during additional deposition of Cs was $1.0\text{--}1.1 \times 10^{-7}$ Pa.

Fig. 11 Common logarithm of normalized photocurrent as a function of elapsed time from 0 to 190 h in lifetime test of Cs₃Sb photocathode in experiment II. The intensity of the 405 nm laser at the cathode tip during continuous laser irradiation and continuous electron emission, the vacuum level, and the time of W deposition are shown.

Fig. 12 Common logarithm of normalized photocurrent as a function of elapsed time from 190 to 347 h in lifetime test of Cs₃Sb photocathode in experiment II. The intensity of the 405 nm laser at the cathode tip during continuous laser irradiation, and the vacuum level are shown. This figure continues Fig. 11.

Fig. 13 Common logarithm of normalized photocurrent as a function of elapsed time from 0 to 250 h in lifetime test of Cs_3Sb photocathode in experiment VII. The vacuum level, and the times of additional Cs deposition and Cr deposition are shown.

Fig. 14 Common logarithm of normalized photocurrent as a function of elapsed time from 250 to 455 h in lifetime test of Cs_3Sb photocathode in experiment VII. The intensities of the 405-nm laser at the cathode tip during the continuous laser irradiation, and the vacuum level are also shown. This figure continues Fig. 13.