Full length article

Research on activation mechanism of AlGaN photocathodes in an ultra-high vacuum system

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ABSTRACT

At present, most of the III-V semiconductor photocathodes, such as GaAs, GaN and AlGaN photocathodes are activated by Cs/O at room temperature. In order to analyze the influence of different activation conditions on the performance of AlGaN photocathode, and investigate the mechanism of surface activation, five AlGaN photocathodes were activated with different conditions in an ultra-high vacuum system under a pressure of 10^{-8} Pa. Three samples were activated by Cs/O under different temperatures at room temperature (about 25 °C), high temperature (about 60 °C) and low temperature (about −50 °C), respectively. One sample was activated by Rb/O at room temperature. Besides, one more sample was activated by Cs/O at room temperature to study the stability of AlGaN photocathode after activation. The results show that the performance of AlGaN photocathode could be affected greatly by activation conditions, and the mechanism was analyzed. The effect of excessive Cs treatment after activation on the stability of AlGaN photocathode was studied.

1. Introduction

Ultraviolet (UV) detection technology has been widely used in many fields, especially in the mid-ultraviolet wavelength band of 220–280 nm. At present, image intensifiers based on alkali metal tellurides photocathodes (Cs_2Te and Rb_2Te) are the main detectors. In recent years, the negative electron affinity (NEA) AlGaN photocathodes have been actively developed. It is expected that the quantum efficiency of AlGaN photocathode can be higher than that of the alkali metal telluride photocathodes. Many studies on GaN-based photocathodes were reported [1–8]. So far, AlGaN photocathodes have also made great progress, achieving good quantum efficiency and spectral response [9–12].

The performance of photocathode is greatly affected by the activation methods. A few of research work has been done on the activation of GaN photocathodes [13–15]. However, most reports are concentrated in the activation of Cs/O at room temperature. And few studies have been reported on the activation of AlGaN photocathodes under different conditions. In this paper, five AlGaN photocathodes were activated with different conditions after the same chemical treatment and high temperature cleaning, and the surface activation mechanism has been investigated. Three samples were activated by Cs/O under different temperatures at room temperature (about 25 °C), high temperature

(about 60 °C) and low temperature (about −50 °C), respectively. And one sample was activated by Rb/O at room temperature. The results show that the performance of AlGaN photocathode could be affected greatly by activation conditions, and the mechanism was analyzed. Besides, one more sample was made to study the stability of AlGaN photocathode after Cs/O activation at room temperature, and the results show that excessive Cs treatment after Cs/O activation of AlGaN photocathode can effectively improve the stability of photocathode.

2. Preparation

Five samples of AlGaN photocathode materials were grown one time by Metal Organic Chemical Vapor Deposition (MOCVD). The structure of AlGaN photocathode is shown in Fig. 1, which is the same with ref. [12]. A band-gap width gradient was formed in the body of the material. The gradient band-gap makes an effective built-in electric field formed inside the material, and it can effectively enhance the electron diffusion length and the quantum efficiency of AlGaN photocathode.

The five AlGaN materials were cut down to wafers with 20 mm diameter using a laser cutter, and then were cleaned. The cleaning method includes chemical treatment and high temperature (700 °C) cleaning treatment in vacuum environment, which is the same with ref.

Fig. 1. Structure of the AlGaN photocathode.

Sample number	Activation resources	Activation temperature
1#	Cs, O	about 25 °C
2#	Cs, O	about 60 °C
3#	Cs, O	about −50 °C
4#	Rb, O	about 25 °C
5#	Cs, O	about 25 °C

[12]. The AlGaN photocathode was activated after heat cleaning. The schematic diagram of AlGaN photocathode activation in vacuum chamber is shown in Fig. 2. The deuterium lamp is straight on the top of the AlGaN photocathode, the photocurrent collector and the Cs, Rb and O source are under the AlGaN photocathode, and the temperature measuring thermocouple is at the same height with the AlGaN photocathode.

The Cs, Rb and O is released into the activation chamber by regulating the heating current of the nickel tube, and the heating currents are 3.25 A, 2.35 A and 1.61 A, respectively. During the activation, the deuterium lamp was irradiated on the surface of the AlGaN photocathode, and the light power of the deuterium lamp is 100 W. And the photocurrent was collected on-line to observe the change of the photocurrent, and the collecting voltage is 200 V. In the activation process, the Cs or Rb source is turned on continuously, and the O source was turned on or off periodically according to the photocurrent variation. The whole activation process is under a pressure of 10^{-8} Pa in the ultra-high vacuum chamber.

The five AlGaN photocathode samples were marked as 1#, 2#, 3#, 4# and 5#, and the activation conditions are shown in Table 1.

The sample 1# and 5# were activated by Cs/O at room temperature about 25 °C. The sample 2# was activated by Cs/O at a higher temperature, the vacuum chamber was heated by heating belts all the time during the activation process, and the internal temperature was stable at about 60 °C. The sample 3# was activated by Cs/O at a lower temperature, the vacuum chamber was cooled by liquid nitrogen in the interlayer of the chamber all the time during the activation process, and the
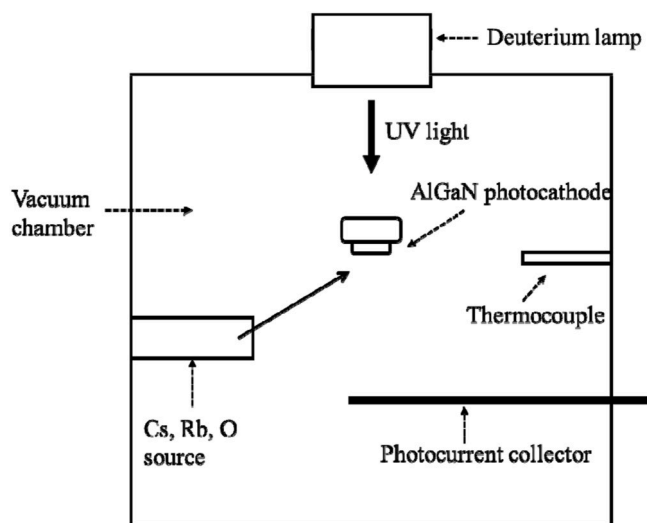
internal temperature was stable at about −50 °C. The sample 4# was activated by Rb/O at room temperature.

3. Results and discussion

The photocurrent curves of AlGaN photocathodes activated by Cs/O under different temperatures are shown in Fig. 3. During the activation, the first stage is the Cs exposure, and the second stage is the Cs/O activation. The first peak of the photocurrent could be reached in the Cs exposure, and then the photocurrent is going to drop when the Cs is in excess on the AlGaN surface. The O source is opened when the photocurrent drops to a valley value, and the second peak of the photocurrent could be reached as the maximum in the Cs/O activation, which means the end of the activation. The first peak photocurrent values, the time reaches the first peak, and the final maximum photocurrent values of the three samples are different greatly, because the three samples were activated under different temperatures.

The final photocurrent value of sample 1# is 1046 nA, and at the end of Cs/O activation, the photocurrent drops fast to a stable value when the O is off, and the photocurrent recovers quickly to a higher value after the Cs is off. In the second stage of the activation, the O may be slightly in excess, after the Cs is off, with the continuous desorption of Cs from the surface of AlGaN, the ratio of Cs to O reaches a more optimal value, and the photocurrent reaches a higher value than before. In Fig. 3, the sample 2# is activated at a high temperature, the first peak photocurrent value in the Cs exposure of sample 2# is the maximum of the three samples. However, the photocurrent of sample 2# increases a less in the following Cs/O activation. For sample 3#, the activation temperature is low, the first peak photocurrent value of Cs activation is the minimum, while the photocurrent increases obviously in the Cs/O activation. However, the final photocurrent value of sample 3# is the smallest, which may be induced by a low activity of Cs and O atoms. At the end of the Cs/O activation, the photocurrent drops very fast when the O is off, and it recovers very slowly after the Cs is off.

The photocathode activation photocurrent curves by Cs/O and Rb/O at room temperature are shown in Fig. 4.

Fig. 2. The schematic diagram of AlGaN photocathode activation in vacuum chamber.
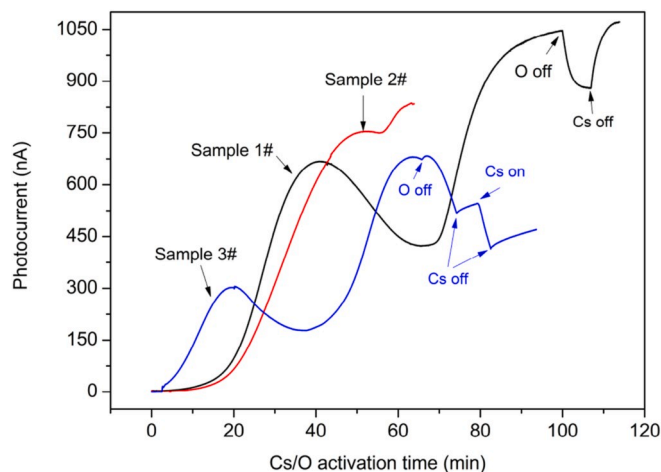

Fig. 3. Photocurrent curves during activation by Cs/O under different temperatures.

As we can see from Fig. 4, the Rb/O activation process is similar as the Cs/O activation, the first peak photocurrent value of the sample 4# is slightly less than the sample 1#. However, the final photocurrent value of sample 4# is much less than that of sample 1#. The first peak photocurrent values, the valley photocurrent values, the time reaches the first peak photocurrent, and the final photocurrent values are summarized in Table 2.

When the AlGaN materials are exposed in the Cs or Rb sources, the Cs or Rb atoms would be adsorbed on the AlGaN surface, and the surface potential energy of AlGaN decreases gradually with the photocurrent increasing by the time till to the peak. The surface potential energy of AlGaN increases as the "Cs kill" phenomenon when the Cs or Rb atoms on AlGaN surface are in excess, which makes the photocurrent decrease. Because of the wide bandgap of AlGaN material, the surface potential energy increases to a certain stable value in excessive Cs or Rb with the photocurrent dropping to the valley value. The bandgap of AlGaN is about 4.1 eV when the Al content is 0.3, and the increase of the surface potential energy due to the excessive Cs or Rb is small compared to the bandwidth of AlGaN, when the surface potential energy increases to the maximum, the photocurrent reduces to the valley and stays at a large value. When the O is turned on, the O atoms begin to react with the Cs or Rb atoms to form a dipole layer on the AlGaN surface. The surface potential energy could be further reduced to a lower level after the adsorption of O atoms, and the photocurrent increases to the maximum in the end.

In Fig. 3, the sample 2# is activated at a high temperature, the results show that a higher temperature, a greater desorption energy of Cs, and the background pressure is relatively worse. In the first stage of activation, the Cs atoms are easier to desorb from AlGaN surface when the activation temperature is high, and less Cs atoms could be accumulated on AlGaN surface, so the "Cs kill" phenomenon caused by Cs atom stacking is not obvious. In the meanwhile, the activity of residual gas molecules in the vacuum chamber is strong, which enhances the adsorption talent of gas molecules such as CO, CO_2, and H_2O on AlGaN surface. In the exposure of Cs, the Cs would react with oxide molecules and form Cs–O dipoles, which causes a high photocurrent in the process of Cs activation. However, the residual C and H atoms would prevent photoelectrons emit into vacuum. In the process of Cs/O activation, the oxide molecules have replaced the role of O atoms, and decrease the adsorbing capacity of O atoms. And the residual C and H atoms would prevent the Cs–O dipoles form. So, the effect of Cs/O activation is smaller than the photocathodes activated at room temperature.

The sample 3# is activated at a low temperature, the ionization rate of Cs on AlGaN surface would be decreased. The stacking Cs atoms on surface would prevent photoelectrons emit into vacuum. So, the peak photocurrent in the exposure of Cs is lower than that of Sample 1#. In the Cs/O activation, the O atoms would react with stacking Cs atoms and form Cs–O dipoles, which makes photocurrent have a lager percent of increasing. Due to a low temperature, the activity of oxide molecules also decrease, which would have a less effect on activation in comparison of sample 1#.

The escape work function of Cs is 2.14 eV, which is slightly lower than the one of Rb. Therefore, the AlGaN activated by Cs/O could obtain a lower surface potential energy than the photocathode activated by Rb/O, which is the main factor that a higher photocurrent value of AlGaN photocathode activated by Cs/O. The band structure of AlGaN photocathode activated by Cs/O and Rb/O based on the double-dipole model is shown in Fig. 5. The photoelectrons excited from the valence band of AlGaN photocathode with a graded Al composition structure would diffuse and drift to the surface because of the electron concentration gradient and the built-in electric field. A comparison of Rb/O and Cs/O surface barriers indicates a lower surface barrier could make more electrons tunnel into vacuum. In contrast with the Rb/O activated photocathode, the Cs/O activated photocathode has a lower barrier I and II, because the Cs atom has a lower escape work function.

After activation, when the Cs and O are turned off, the Cs atoms would desorb from the AlGaN surface in the open vacuum system [16, 17], leading to the photocurrent decrease gradually. The lifetime of image intensifier is greatly influenced by the stability of AlGaN photocathode after activation. The photocurrent of the sample 1# could recover quickly to a higher value with excessive Cs treatment after Cs/O activation in Fig. 3. One more AlGaN photocathode marked as sample 5# was made to study the stability of AlGaN photocathode after Cs/O activation without excessive Cs treatment. The photocathode activation photocurrent curves of sample 1# and 5# is shown in Fig. 6. The excessive Cs treatment means the photocurrent reduces to a stable value when the O is off at the end of Cs/O activation, as the photocurrent curve of sample 1# shown in Fig. 6. The activation process of sample 5# is very close to sample 1#, when the maximum photocurrent value of sample 5# was obtained at 970 nA, the Cs and O were turned off at the same time.

After activation, the photocurrent was recorded every 3 min. For sample 1#, the first point is the maximum photocurrent after recovering, and the value is 1071 nA. For sample 5#, the first point is the photocurrent at the end of activation, and the value is 970 nA. The first point records of sample 1# and sample 5# are marked out in Fig. 6. The reduction ratio is the ratio of the photocurrent value to the maximum photocurrent value for both samples. The comparison of reduction ratio of sample 1# and sample 5# is shown in Fig. 7.

As we can see from Fig. 7, the photocurrent of sample 1# decreases slowly, while the photocurrent of sample 5# decreases faster than sample 1#, especially in the first several minutes. The desorption of Cs from AlGaN surface is fast in the first several minutes after activation. And the residual gasses such as CO_2, H_2O and CO could influence the stability of AlGaN photocathode in the ultra-high vacuum chamber. The residual gas molecules adsorbed on the photocathode surface would damage the original NEA surface. The assumption about activity region is mentioned by Whitman [18]. So, we assume the NEA surface layer is constituted by a lot of activity regions. Once a harmful gas molecule adsorbs on an activity region, the original dipole of activity region would be damaged and the talent of photoemission would decrease.

We assume the number of activity region per unit area of NEA AlGaN photocathode is *N*. When the vacuum pressure is *P*, the collision times of harmful gas molecule on the photocathode surface per unit area, per unit time, per unit of light intensity are HR_cP, R_c is collision coefficient, the light intensity is *H*. The degradation coefficient of activity region affected by harmful gas molecule is *A*. At time *t*, the ratio of the residual activity region per unit area and the total activity region per unit area is $\theta(t)$.

According to the assumption above, the photocurrent of photocathode with time *I*(t) is could be given by [19].
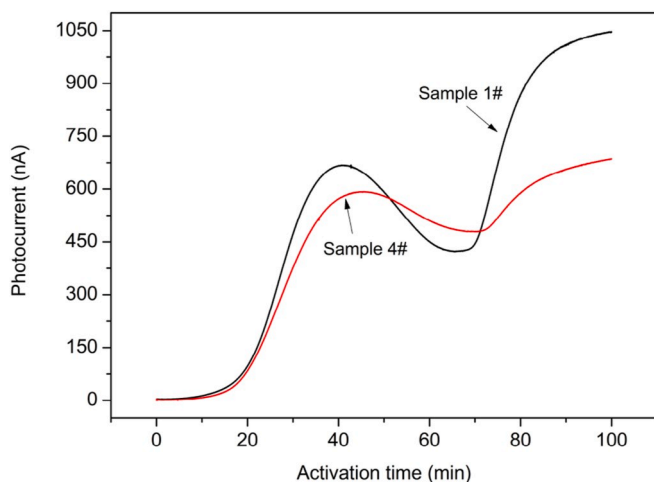

Fig. 4. Photocurrent curves during activation by Cs/O and Rb/O at room temperature.

Table 2
Activation data of AlGaN photocathode samples from 1# to 4#.

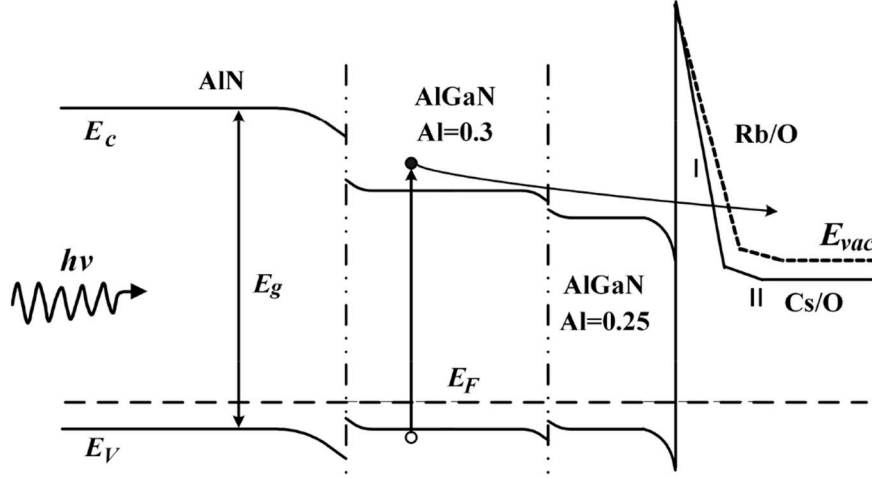| Sample number	The first peak photocurrent value (nA)	The valley photocurrent value (nA)	The valley photocurrent value/the first peak photocurrent value	The time reaches the first peak photocurrent (min)	The final photocurrent value (nA)	The final photocurrent value/the first peak photocurrent value
1#	667	422	0.63	41	1046	1.57
2#	753	749	0.99	52	834	1.11
3#	305	178	0.58	20	680	2.23
4#	592	479	0.81	44	686	1.16

Fig. 5. Band structure of AlGaN photocathode activated by Cs/O and Rb/O. E_c is the conduction band minimum, E_v is the valence band maximum, E_F is the fermi level, E_{vac} is the vacuum level.
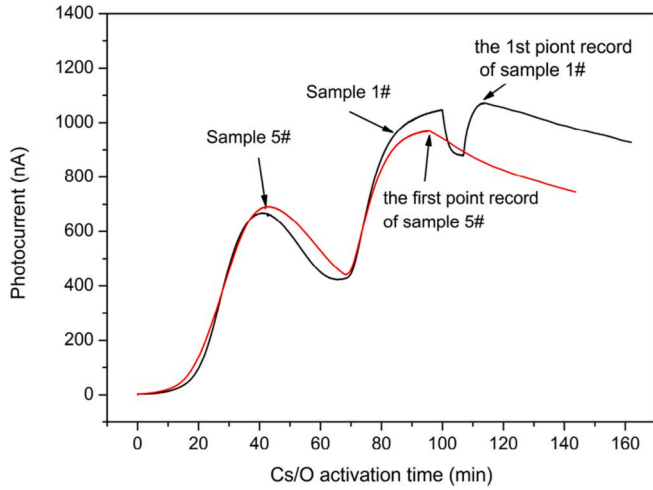

Fig. 6. Photocurrent values during activation of sample 1# and sample 5#.

Fig. 7. Comparison of reduction ratio of sample 1# and sample 5#.

$$I(t) = I_0 \theta(t) \tag{1}$$

$$\theta(t) = \left(1 - \frac{AHR_C P}{N}\right)^t \tag{2}$$

$$I(t) = I_0 \left(1 - \frac{AHR_C P}{N}\right)^t \tag{3}$$

From Eq. (3), it could be found that the photocurrent degraded with time is in the form of exponential approximately, and the degraded formula could be described by,
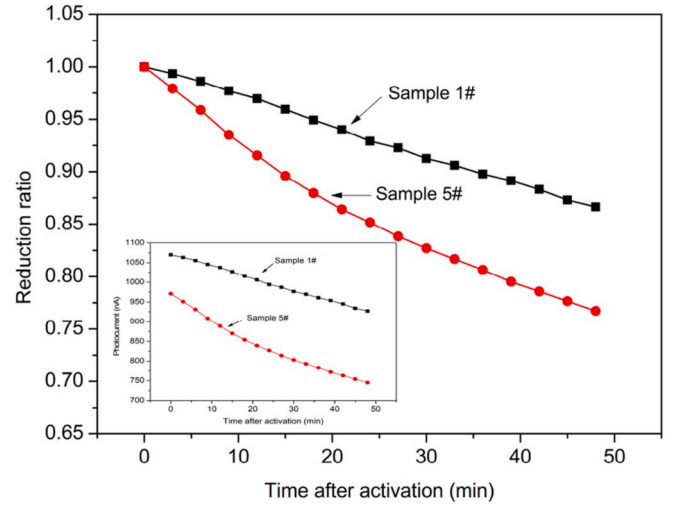
$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right) \tag{4}$$

$$\tau = -\frac{1}{\ln\left(1 - \frac{AHR_C P}{N}\right)} \approx \frac{N}{AHR_C P} \quad \frac{AHR_C P}{N} << 1 \tag{5}$$

From Eq. (5), it could be found that the lifetime of photocathode is proportional to the number of activity regions on the surface, and is inverse proportional to the collision coefficient and the degradation coefficient affected by harmful gas molecule.

In Fig. 7, Sample 1# has a longer lifetime in comparison of sample 5#. For sample 1#, the excessive Cs atoms exist on the surface after activation. In the process of reduction, the excessive Cs atoms would react with the O ions of the oxide molecules and form new Cs–O diploes.

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However, the residual atoms such as C and H atoms would make activity regions disabled. For sample 5#, there are no Cs–O diploes forming in the reduction process. So, we can conclude the degradation coefficient *A* of Sample 1# with an excessive Cs surface is smaller than that of sample 5#. Therefore, excessive Cs treatment after activation can effectively improve the stability of AlGaN photocathode.

4. Conclusion

In this article, five samples of AlGaN photocathode materials were grown one time by MOCVD. After the same chemical treatment and high temperature (700 °C) cleaning treatment in vacuum environment, the samples 1#, 2# and 3# were activated by Cs/O under different temperatures. The sample 4# was activated by Rb/O at room temperature, and the sample 5# was activated by Cs/O to study the stability of AlGaN photocathode after activation. The results show that the desorption energy of Cs is greatly affected by the temperature, a higher the temperature, a greater the desorption energy of Cs. When the photocathode is activated at a high temperature, few Cs atoms can react with O to form a dipole layer on AlGaN surface. And the photocurrent could be influenced greatly by residual gas molecules in the vacuum chamber such as CO, CO_2, and H_2O. However, when the photocathode is activated at a low temperature, the photocurrent is small due to a low activity of Cs and O atoms. When the AlGaN photocathode is activated by Rb/O, the surface potential energy of AlGaN is higher than activated by Cs/O. Therefore, the photocurrent values activated under other conditions are much lower than that of sample 1#. The stability of AlGaN photocathode after activation was studied, the results show that excessive Cs treatment after activation can effectively decrease the degradation rate of surface dipoles, which improves the stability of AlGaN photocathode.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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