Comparison of the photoemission behaviour between negative electron affinity GaAs and GaN photocathodes*

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In view of the important application of GaAs and GaN photocathodes in electron sources, differences in photoemission behaviour, namely the activation process and quantum yield decay, between the two typical types of III–V compound photocathodes have been investigated using a multi-information measurement system. The activation experiment shows that a surface negative electron affinity state for the GaAs photocathode can be achieved by the necessary Cs–O two-step activation and by Cs activation alone for the GaN photocathode. In addition, a quantum yield decay experiment shows that the GaN photocathode exhibits better stability and a longer lifetime in a demountable vacuum system than the GaAs photocathode. The results mean that GaN photocathodes are more promising candidates for electron source emitter use in comparison with GaAs photocathodes.

Keywords: III–V photocathode, negative electron affinity, Cs–O activation, quantum yield decay

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1. Introduction

III–V negative electron affinity (NEA) photocathodes have already found widespread applications in vacuum detecting devices and polarized electron sources because of their high quantum efficiency, low dark current emission and narrow energy spread qualities.[1−4] As the two main types of III–V compound semiconductors, GaAs and GaN photocathodes have attracted extensive attention due to their respective use as low-light visible detectors and solar-blind ultraviolet detectors because of their different band gaps.[5−8] More recently, GaAs and GaN photocathodes have become more important in their applications in electron sources and a major requirement for a photocathode that can achieve a higher quantum efficiency and a longer lifetime in a demountable vacuum system are pressing.[9,10] In view of this, there is a need for comparison of the photoemission behaviour between GaAs and GaN photocathodes.

To achieve an NEA state, the semiconductor surface should be activated by means of deposition of cesium and oxygen on a clean surface. As a result of the decline of surface vacuum level, an effective NEA state that enables thermalized electrons to escape from the surface is obtained when the vacuum level at the surface is below the conduction band minimum in the bulk of the material.[11] Although some similar characteristics exist in the preparation of NEA GaAs and GaN photocathodes, little work has been published on the comparison of their differences in photoemission behaviour, such as the activation and degradation processes under similar preparation conditions between the two types of photocathodes in early studies. In this paper, we investigate the activation process and lifetime degradation of reflection-mode GaAs and GaN photocathodes both grown by metalorganic chemical vapor deposition (MOCVD) using a self-developed multi-information measurement system. In addition, the remarkable difference in the photoemission mechanism between GaAs and GaN photocathodes is analysed in detail.

2. Experiment

Two types of reflection-mode GaAs and GaN photocathode samples were grown by MOCVD. The major difference in the grown structure is as follows: the GaAs photocathode sample has a 0.8-μm thick p-type

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blende GaAs (100) active layer with Zn-doping concentration of 1.0×10^{19} cm^{-3}, which is grown on an AlGaAs buffer layer and a p-type GaAs (100) substrate, while the GaN photocathode sample has a 0.15-μm thick wurtzite GaN (1000) active layer with Mg-doping concentration of 1.6×10^{17} cm^{-3} grown on an AlN buffer layer and a c-axis sapphire substrate. In the two grown structures, the buffer layer (AlGaAs or AlN layer) ensures a smooth surface for the epitaxial active layer and also serves as an electron mirror that can reflect the back diffusion electrons towards the vacuum surface. In view of the discrepancy in the electron diffusion length between GaAs and GaN, the designed thickness of the GaAs active layer on the order of micron was larger than that of the GaN active layer on the order of nanometer.[12,13]

Prior to the activation process, as there is a need for an atomically clean crystal surface, the photocathode must undergo a two-step surface preparation consisting of a wet chemical cleaning process and a heat treatment process in vacuum to eliminate surface contaminates such as carbon and oxides. Both the GaAs and GaN samples were etched by a H_2SO_4:H_2O_2:H_2O solution with different ratios of 4:1:100 for 1 min and 2:2:1 for 10 min because of the different etching ability.[14,15] After being rinsed by deionized water and dried in air, the samples were transferred to a ultra-high vacuum (UHV) chamber with a base pressure less than 10^{-7} Pa and heated in vacuum at 650 °C (GaAs) and 710 °C (GaN) for 20 min periods. The cathode was heated by a halogen lamp and the temperature of the sample was monitored by a thermocouple.

When the heat cleaned samples cooled to room temperature, the NEA activation was performed with an improved activation technique called co-deposition activation,[16] in which a cesium source was kept continuously and oxygen source was introduced periodically. The Cs source used in the activation is in the form of a mixture of cesium chromate and zirconium–aluminum alloy powder in a thin-walled nickel tube and the oxygen source is in the form of barium peroxide in a nickel tube. The operating current of the Cs and O sources, and the photocurrent from the cathode during the NEA activation process were controlled and monitored by a self-developed multi-information measurement system, as shown in Fig. 1. The vacuum in the UHV chamber was monitored by a vacuum gauge and a quadrupole mass spectrometer (QMS).

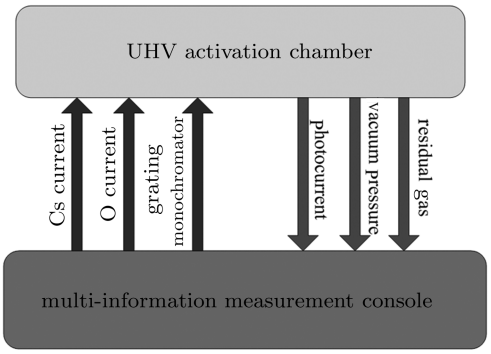


Fig. 1. Schematic drawing of the multi-information measurement system for NEA photocathode preparation.

For the whole activation process, the initial Cs deposition on the cathode samples was made with a vacuum pressure reaching 1.4×10^{-7} Pa. After the first maximum photoemission current was surpassed, continuing the cesiation, we turned on the oxygen when the photocurrent dropped to 85% of the first maximum value or the maximum lasted for ten minutes without drop. During the Cs–O alternate activation cycles, the vacuum pressure range was kept in the range from 1.4×10^{-7} Pa to 2.2×10^{-7} Pa. For both the GaAs sample and GaN sample, the Cs/O flux ratio was adjusted to the same value of 1.75/1.65. Until there was no increase in the photocurrent peak, the O flux and Cs flux were closed in turn, and then the decay of quantum yield for the activated photocathodes under a monochromatic beam light was measured to compare the stability and lifetime of the NEA GaAs and GaN photocathodes in a demountable vacuum chamber. Because of the different sensitive light regions of interest, the illumination source for the GaAs photocathode was a halogen tungsten lamp set at (600 ± 5) nm with a 24-μW optical power of a 5-mm diameter spot through the grating monochromator, while a xenon lamp set at (300 ± 5) nm with a 50-μW optical power of a 5-mm diameter spot through the grating monochromator was used for the GaN photocathode. The decay of quantum yield with time for the photocathodes was obtained by calculating the ratio of the measured photocurrent to the irradiating optical power.

3. Results and discussion

3.1. Cs–O alternate activation

The entire process consisting of Cs-only and Cs–O alternate activation for both the GaAs and GaN samples with the same Cs/O flux ratio is shown in Fig. 2. For GaAs, there is no "Cs kill" phenomenon

that the first photocurrent maximum would drop at the stage of initial Cs exposure, while GaN sample is different: it is easy to get over-cesiuminizd. Besides, the Cs–O activation cycles of the GaAs sample can cause the final photocurrent maximum to increase by a factor of seven in contrast to Cs-only activation. Unlike GaAs, the Cs–O activation cycles for the GaN sample cause no further improvement in the photocurrent maximum. There are only two Cs–O activation cycles for increasing the photocurrent maximum by approximately 20%. It is thus concluded that successful activation of a GaAs photocathode requires Cs–O alternate activation, while the activation of a GaN photocathode can just rely on Cs-only activation.

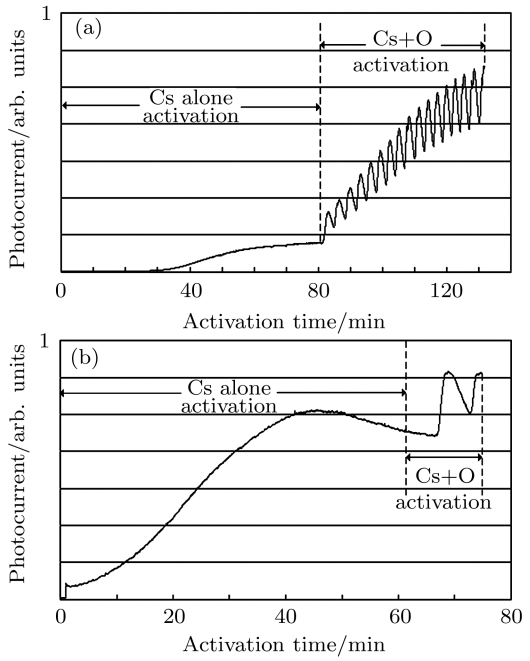


Fig. 2. Cs–O activation curves of (a) GaAs photocathode and (b) GaN photocathode.

The striking difference in the activation process between the GaAs and GaN photocathodes can be explained by comparing of the energy band structures and calculating the reduction of electron affinity. The effective electron affinity $\chi_{\rm eff}$ is defined as the energy difference between the vacuum level and the conduction band minimum in the bulk of the material. Through Cs-only deposition or the Cs–O co-deposition on the cathode surface, the $\chi_{\rm eff}$ is lowered to a negative state so as to facilitate the electrons crossing surface potential barrier and escape into vacuum. A Topping model represents the relation between electron affinity reduction and the adatom-induced surface dipoles, and is given by[17]

$$\Delta\chi = -\frac{ep\theta}{\varepsilon_0}\left(1+\frac{9\alpha_{\rm ad}\theta^{3/2}}{4\pi\varepsilon_0}\right)^{-1}, \qquad (1)$$

where e is the electronic charge, p is the dipole moment of the adatom-induced dipoles, ε_0 is the permittivity of vacuum and $\alpha_{\rm ad}$ is the polarizability of the adatoms, and θ is the surface coverage of adatoms. Based on the Topping model, the changes in effective electron affinity of the GaAs and GaN surfaces as functions of Cs coverage are shown in Figs. 3(a) and 3(b), respectively. The experimental data are determined by energy distribution curve (EDC) measurement.[18,19] From the theoretical and experimental data, we can know that the photocurrent reaches the first maximum at a Cs coverage of approximately 0.6 monolayer (ML) for GaAs and 0.75 ML for GaN, when $\chi_{\rm eff}$, as the Cs coverage increases, is decreased to the minimum. After Cs-only activation, the GaAs cathode surface exhibits a positive electron affinity (PEA) state with a vacuum level drop of 3.4 eV, while the GaN cathode surface exhibits a NEA state with a vacuum level drop of 3.0 eV. After oxygen is admitted onto the Cs adsorbed surface, the surface $\chi_{\rm eff}$ is further decreased to a –0.5 eV NEA state for the GaAs photocathode and a –1.2 eV NEA state for the GaN photocathode.[19,20]

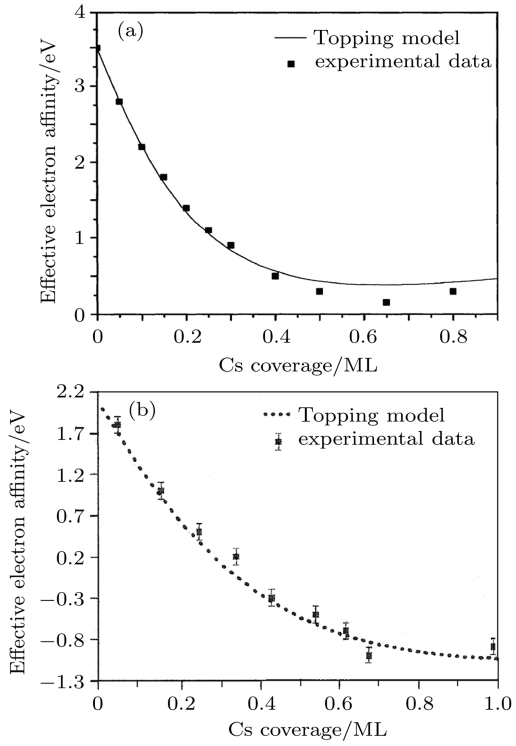


Fig. 3. Variation in effective electron affinity of (a) the GaAs photocathode and (b) the GaN photocathode with increasing Cs coverage at room temperature (after Refs. [18] and [19]).

The band structure variations of the GaAs and GaN photocathodes during the activation process are shown in Figs. 4(a) and 4(b), respectively: the experimental phenomenon indicates that as the band gap

increases, the surface potential barrier to vacuum decreases, requiring a smaller change in the vacuum level position relative to the bulk conduction band minimum to achieve an NEA emitter. This implies that the NEA activation of the wide band gap GaN photocathode is achieved more readily in comparison with that of the small band gap GaAs photocathode. For a GaN photocathode, with Cs-only activation, the vacuum level is lowered to an NEA state and the addition of oxygen changes $\chi_{\rm eff}$ by a few tenths of an electron volt. consequently the introduction of oxygen to the Cs-only dipole layer to form a cesium oxide dipole layer does not provide a significant enhancement in the decrease of the vacuum level. Whereas for GaAs photocathode, the emitter has a PEA state with Cs-only deposition, and admission of oxygen is necessary to obtain the NEA emission property, which is responsible for the remarkable difference in Cs–O activation cycles between GaAs and GaN photocathodes.

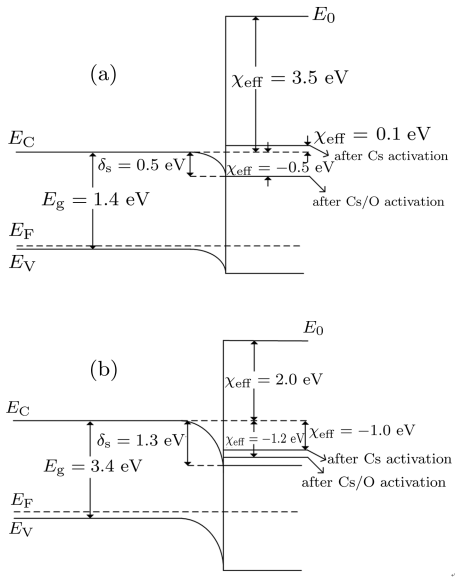


Fig. 4. Schematic energy band variation of (a) the GaAs photocathode and (b) the GaN photocathode surface after Cs-only and Cs/O activations. $E_{\rm C}$ is the conduction band minimum, $E_{\rm V}$ is the valence band maximum, $E_{\rm g}$ is the band gap, $E_{\rm F}$ is the Fermi level, E_0 is the vacuum level and $\delta_{\rm s}$ is the surface-downward band bending energy.

3.2. Quantum yield decay

It is well known that the adsorption of O contained in residual gas such as H_2O, CO and CO_2 in a demountable vacuum system can act on the activated NEA surface and influence photocathode stability.[21,22] During the photocathode lifetime degradation process, the residual gas component monitored by QMS is presented in Fig. 5 with a total vacuum pressure of 1×10^{-7} Pa. As can be seen from Fig. 5, the dominant residual gas in our demountable vacuum chamber is in the region around mass 2, 18, 28 and 44, corresponding to H_2, H_2O, CO and a small quantity of CO_2.

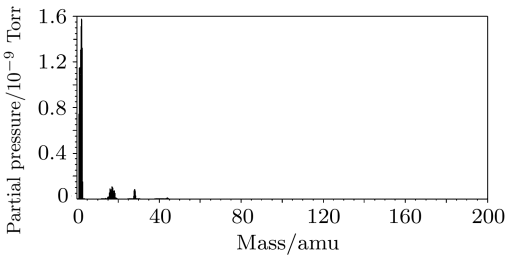


Fig. 5. Residual gas mass spectrum in the UHV chamber during the cathode degradation process. 1 Torr = 1.33322×10^2 Pa.

After Cs–O activation, the maximum quantum yield of the GaAs photocathode at the radiation wavelength of 600 nm reaches about 11%, while that of GaN photocathode at the radiation wavelength of 300 nm achieves 32%. The quantum yield decay of the GaAs and GaN photocathodes under the illumination of monochromatic light are shown in Figs. 6(a) and 6(b), respectively. It can be seen that the GaN photocathode exhibits a higher quantum yield and better stability than the GaAs photocathode. Usually, efficient degradation of the lifetime at room temperature can be obtained by means of $1/e$ lifetime analysis.[23] However, the simulated curve in this form is not consistent with our experimental data, and a relatively stable quantum yield at room temperature is obtained over the degradation period. A fitting formula to the experimental data in Fig. 6 is in the form

$$\eta(t) = \eta_0 + A\exp(-t/\tau), \tag{2}$$

where η_0 is the relatively stable quantum yield, τ is the relatively stable lifetime and A is defined as a degradation coefficient. For both the GaAs and GaN photocathodes, the fitted results are in excellent agreement with the experimental data, as shown in Fig. 6, and the fitted parameters of quantum yield decay are listed in Table 1. Under continuing low light illumination, the quantum yield of the GaAs photocathode decays to 3.5% with decreasing by 70% over a period of 3 hours, while that of the GaN photocathode decays to 16% with decreasing of 50% over a period of 20 hours.

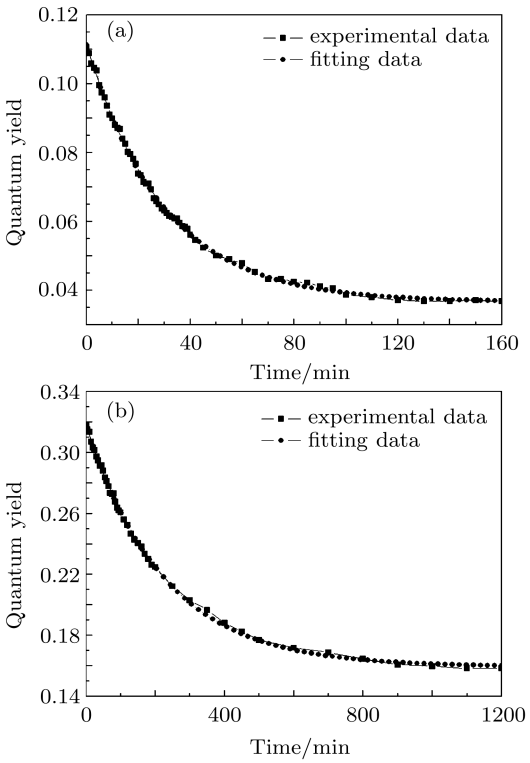


Fig. 6. Quantum yield decay of (a) the GaAs photocathode and (b) the GaN photocathode after activation under continuous monochromatic light illumination.

Table 1. Fitting parameters of quantum yield decay for GaAs and GaN photocathodes.

type	$\eta_{\max}$/%	η_0/%	A/%	τ/min
GaAs sample	11	3.5	7.5	30
GaN sample	32	16	16	226

The reasons for the better stability of the GaN photocathode are as follows: the adsorption of O contained in the residual gas increases the surface potential barrier. It can be seen from Fig. 4 that the GaN photocathode surface returns to a PEA state, requiring changes in the vacuum level at least on the order of one electron volt. For example, in the GaAs photocathode the vacuum level only needs to increase by a few tenths of one electron volt and thus the wide band gap photocathodes can obtain a prolonged operation lifetime in comparison with the small band gap ones. The Cs-induced dipoles on the GaN surface exhibit a more powerful bond than those on the GaAs surface because the N atom in GaN is more electronegative than the As atom in the GaAs. Experiments show that the GaN photocathode surface can still produce a considerable photocurrent after low temperature heat treatment,[24] which is completely different from the GaAs photocathode. Usually, by supplying additional Cs flux at the end of the cathode activation process, the degradation rate can be reduced and the stability of activated photocathodes can be thus enhanced.[19,23] In addition, the vacuum pressure is crucial and the cathode lifetime can be extended by an order of magnitude if the vacuum pressure is improved by an order of magnitude.[22]

4. Conclusion

In this paper, we have investigated the differences in the photoemission behaviour, namely the activation process and quantum yield decay, between GaAs and GaN photocathodes as two typical III–V NEA photocathodes, using a multi-information measurement system. Both samples, grown by the MOCVD method, underwent the same H_2SO_4:H_2O_2:H_2O solution-based chemical cleaning and Cs/O flux ratio based activation process. The results show that a surface NEA state can be achieved by a Cs–O two-step activation necessary for GaAs photocathode, and by Cs-only activation for GaN photocathode. In addition, the GaN photocathode exhibits better stability and a longer lifetime than the GaAs photocathode, which indicates that the GaN photocathode might be a more robust emitter for application in electron sources.

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