Influence of wet chemical cleaning on quantum efficiency of GaN photocathode*

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GaN samples 1–3 are cleaned by a 2:2:1 solution of sulfuric acid (98%) to hydrogen peroxide (30%) to de-ionized water; hydrochloric acid (37%); or a 4:1 solution of sulfuric acid (98%) to hydrogen peroxide (30%). The samples are activated by Cs/O after the same annealing process. X-ray photoelectron spectroscopy after the different ways of wet chemical cleaning shows: sample 1 has the largest proportion of Ga, N, and O among the three samples, while its C content is the lowest. After activation the quantum efficiency curves show sample 1 has the best photocathode performance. We think the wet chemical cleaning method is a process which will mainly remove C contamination.

Keywords: GaN photocathode, X-ray photoelectron spectroscopy, wet chemical cleaning, quantum efficiency

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1. Introduction

GaN is a new type of semiconductor material with excellent characteristics of wide bandgap, low dielectric constant, corrosion resistance, high temperature resistance, and radiation resistance, so it is used widely in optoelectronic and microelectronic devices.[1–7] GaN-based photocathodes show good performance because of their high quantum efficiency (QE), low dark current, and concentrative emitting electron energy distribution.[8–13] Because of the wide bandgap (3.4 eV at room temperature), GaN photocathodes are naturally 'solar blind', and do not respond to visible light, so they have plenty of uses in the fields of ultraviolet detection, fire alarm technology, atmospheric monitoring, lithographic manufacture, and others.[14–18]

GaN photocathodes can be activated by Cs/O in a vacuum to achieve negative electron affinity (NEA), which makes a much higher QE.[19–21] Before activation, the GaN (0001) surface must be cleaned to the atomically clean level,[22] and then Cs atoms can absorb on the surface well to achieve NEA. There are many research works on the GaN (0001) surface cleaning. Machuca *et al*. found that immersion in a 4:1 solution of sulfuric acid (51%) to hydrogen peroxide (30%) followed by 700 °C in a vacuum reduces carbon and oxygen coverage to a few percent of a monolayer.[23] Tracy *et al*. have summarized some of the cleaning methods before, and researched *n*-type and *p*-type GaN (0001) thin film surfaces immersed in HCl and chemically vapor cleaned in flowing ammonia under optimized conditions of 860 °C and 10^{-4} Torr (1 Torr = 1.33322×10^2 Pa) pressure. They reported O 1s and C 1s were not detected after this cleaning process.[24] King *et al*. have reported the lowest oxygen coverage on AlN and GaN surfaces is achieved using HF and HCl, and thermal desorption of carbon contaminants was not observed to be complete until temperatures of > 900 °C.[25]

We believe that, for a different vacuum system and different GaN samples (because of the different doping concentration, doping elements, and growing methods), the cleaning methods should be different, so now a variety of different cleaning methods exist. There is no research on the influence of chemical cleaning on the final QE of an NEA GaN photocathode. In the following, we report our study of three wet chemical cleaning methods by X-ray photoelectron spectroscopy (XPS), and the photocathode performance corresponding to each of the different methods is also researched.

2. Experiment

The GaN samples used in this research were grown by metal–organic chemical vapor deposition (MOCVD) on *c*-axis sapphire substrates with a $Ga_{1-x}Al_xN$ buffer layer. The samples were p-type doped by Mg, and the doping concentration is at 10^{17} cm^{-3}.

Four identical GaN samples were prepared. All of the samples were degreased by carbon tetrachloride, acetone, absolute ethyl alcohol, and de-ionized water for 5 min, respectively. Then sample 1 was cleaned by a 2:2:1 solution of sulfuric acid (98%) to hydrogen peroxide (30%) to de-ionized

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water for 10 min; sample 2 was cleaned by hydrochloric acid (37%) for 10 min; sample 3 was cleaned by a 4:1 solution of sulfuric acid (98%) to hydrogen peroxide (30%) for 10 min; and sample 4 was not treated to act as a reference.

After chemical cleaning, all four samples were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS analyzer of PHI-5300 by Perkin–Elmer is employed in our experiments. All XPS measurements were obtained using Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV). The grazing angle is 75°.

Subsequently, samples 1–3 were transferred into the ultra-high vacuum system (base pressure $\leq 3.3 \times 10^{-8}$ Pa), where they were annealed at the same temperature (710 °C for 20 min, and then GaN samples were activated by Cs/O at room temperature under illumination of the same deuterium lamp, one by one. The photocurrent curves of the GaN samples are shown in Fig. 1. Curves 1–3 correspond to samples 1–3. From Fig. 1 it can be seen the three curves are similar overall, Cs is performed with GaN and the photocurrent reaches a peak. When there is no increase or decrease for about 5 min, keeping Cs constant, O is admitted into the system and the photocurrent grows again. The participation of O makes another peak of the photocurrent, and O is shut off at the peak, after which, under Cs, the photocurrent decreases again. Then opening O again, the photocurrent reaches a peak again. After three or four repetitions, there is no significant increase between the present photocurrent peak and the previous, and the activation is ended. For the curves 1 and 2 there is a jump at about 2 min, which is caused by the opening of the deuterium lamp. Before activation of sample 3, the lamp is turned on already.

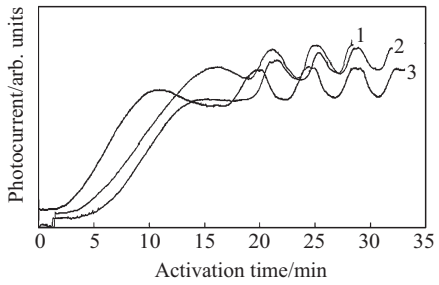


Fig. 1. Photocurrent curves of sample 1–3 during activation.

3. Results and discussion

Spectra were collected from all four samples for the Ga 3d, N 1s, O 1s, and C 1s, as shown in Figs. 2(a)–2(d). The curves have been smoothed automatically, and curves 1–4 correspond to samples 1–4, respectively. Because of an Mg target used, the Ga LMM lines mask the C 1s signal, making it difficult to deconvolute the carbon from the Ga Auger series.

According to the adventitious hydrocarbon C 1s line at 284.8 eV, all other core levels have been charge-corrected. As shown in Table 1, the peak positions and the full width at half maximum (FWHM) of the Ga 3d, N 1s, O 1s, and C 1s are listed, respectively. Ga 3d peaks of GaN and Ga_2O_3 are 19.54 eV and 20.2 eV,[26] respectively, so from the position of the Ga 3d in Table 1 it can be known that Ga_2O_3 exists on all of the sample surfaces. Compared to sample 4, the Ga 3d peak of sample 1 shifts 0.5 eV higher, sample 2 shifts 0.2 eV higher, and sample 3 shifts 0.4 eV higher. The shifts of the Ga 3d peak among the samples show Ga_2O_3 on the surface of sample 1 has a larger proportion than that on the other samples.

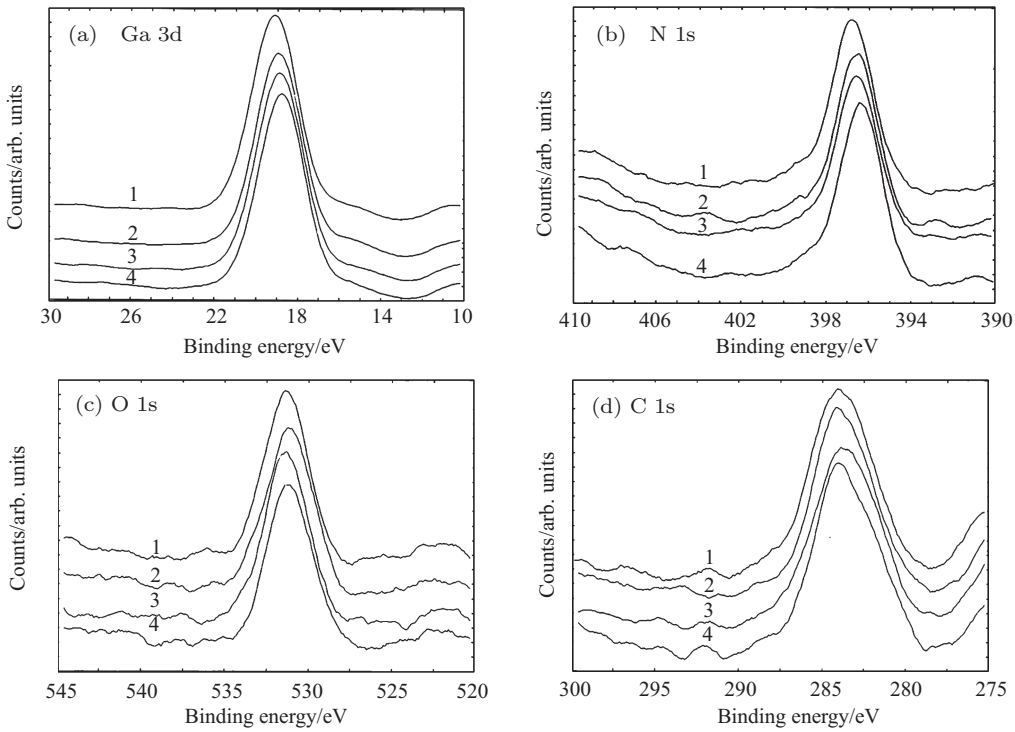


Fig. 2. XPS spectra of the Ga 3d, N 1s, O 1s, and C 1s on GaN (0001). Curves 1–4 correspond to GaN samples 1–4.

Table 1. XPS results for the GaN sample surfaces.

Sample No.		Ga 3d	N 1s	O 1s	C 1s
1 (±0.1 eV)	Center	20.0	397.6	532.1	284.8
	FWHM	2.9	2.6	3.9	4.8
2 (±0.1 eV)	Center	19.7	397.2	531.9	284.8
	FWHM	2.7	2.6	3.7	4.6
3 (±0.1 eV)	Center	19.9	397.6	532.3	284.8
	FWHM	2.8	2.5	3.2	5.1
4 (±0.1 eV)	Center	19.5	397.1	532.0	284.8
	FWHM	2.8	2.5	2.5	4.7

The concentrations of Ga, N, O, and C on the surface of GaN samples, expressed in percentage, are listed in Table 2. Because the C 1s peak contains the signal of the Ga LMM, it is much greater than the actual, and the concentration of C appears to be much more than the actual value. Nevertheless, we can compare the atomic concentration among the different GaN samples. The ratio of Ga/N for all the samples is bigger than 1, which agrees with GaN (0001) surface. As Table 2 shows, the concentration of Ga increases from sample 4 to 1, and sample 1 also has the largest concentrations of N and O, while its C content is the lowest. The lowest concentration of Ga appears on sample 4. Sample 3 has the largest concentration of C, and the lowest of N and O. From Table 2 it can be seen that sample 1 has the cleanest surface except for some gallium oxide. The surface of sample 3 contains the most contamination after cleaning–even worse than sample 4.

Table 2. Atomic concentration (%) of elements on the GaN surfaces measured by XPS.

Sample No.	Ga	N	O	C
1 (%)	19.78	13.55	13.31	53.36
2 (%)	19.03	12.28	13.04	55.65
3 (%)	18.47	12.13	11.51	57.89
4 (%)	18.00	12.30	12.29	57.41

The QE curves of GaN samples 1–3 are shown in Fig. 3. Because no chemical cleaning had been done for sample 4, it was not activated. From Fig. 3 it can be seen that sample 1 has the highest QE, while sample 3 has the lowest. The maximum QE of sample 1 reaches 29% at 5.17 eV. The QE curve of sample 2 is as high as sample 1 at 3.4 eV, but with increasing photon energy, the QE of sample 2 grows slower than sample 1, and the maximum QE reaches 26% at 5.17 eV. The QE curve of sample 3 is lower than that of sample 1 across the whole response wavelength, and the maximum QE reaches 22% at 5.17 eV.

Previous research indicated that successful activation of a GaN photocathode needs an atomically clean surface, and both C and O contaminations should be reduced to the smallest proportions.[15–21] In our experiments, sample 1 has the best performance. After wet chemical treatment XPS results show that sample 1 has the largest proportion of Ga and N while it has the smallest proportion of C, which matches the cleanest surface, but sample 1 also has the largest proportion of O, which needs to be discussed further.

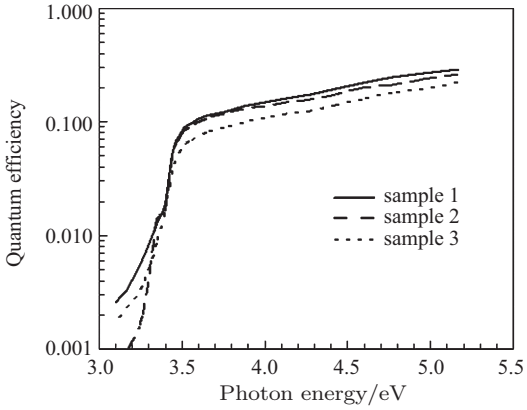


Fig. 3. QE curves of the GaN samples.

The surface cleaning includes chemical cleaning and annealing in two processes. Chemical solution is used to etch the surface of GaN, and oxides of carbon are chemically shifted toward higher binding energy with regard to the hydrocarbon feature.[23] Gallium oxide and other oxides will decompose when GaN is heated to a certain temperature.

As for the influence of the chemical cleaning on the p-type doping of the GaN samples, we think it is too slight to consider. In our experiments, the Mg doping concentration of the GaN sample is 10^{17} cm^{-3}, and the atomic concentration of wurtzite GaN is 8.9×10^{22} cm^{-3},[27] which means there is only one Mg in 10^5 Ga and N, so the proportion of the doping atomic Mg is very small to the total number of atoms. There is even no Mg signal in the XPS spectrum, so the influence on the p-type doping during the chemical cleaning has not been considered.

If the chemical cleaning process has not been carried out completely, the following heating process cannot clean the surface to a satisfactory level. XPS results show that the wet chemical treatment on sample 3 is the least effective, and after the same annealing and activation, sample 3 has the worst performance, which proves the importance of the chemical cleaning process. In future, we will research the surface composition of GaN (0001) during the heating process and how the performance of photocathodes depends on different heating methods.

4. Conclusion

In conclusion, we have researched three wet chemical cleaning methods by XPS, and compared the QE curves corresponding to the different ways of cleaning. Experimental results show that despite some gallium oxide, the sample cleaned by the 2:2:1 solution of sulfuric acid (98%) to hydrogen peroxide (30%) to de-ionized water has the cleanest surface, and

this sample has the highest QE after activation, so a better wet chemical cleaning method was found.

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