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In situ Heating and Thermal Effects in Auger Electron Spectroscopy for GaN

Fu-chun Xu[a,b*], Qi-he Zhang[a], Dan-xia Cen[a]

a. Analysis and Testing Centre, b. Department of Physics, Xiamen University, Xiamen 361005, China

(Dated: Received on March 18, 2005; Accepted on June 24, 2005)

An *in situ* heating system was built for the Auger electron spectroscopy to investigate the thermal effect of Auger lines. A GaN sample was studied in this system. The kinetic energy of Ga LMM and MVV Auger lines were observed to shift negatively with temperature increasing. By using *ab initio* calculation, the theoretical Ga MVV Auger line shape was fit, which well reflects the inner property of the line. The Auger shift with heating is related with the valence electron rearrangement in the thermal expansion of the local bonds.

Key words: Ultra-high-vacuum, Auger electron spectroscopy, Heating system, *In situ*, Auger line shape

I. INTRODUCTION

Auger electron spectroscopy (AES) developed from Auger effect has long proved itself a powerful technique in surface and interface analysis [1]. In virtue of high spatial resolution (25 nm) and high chemical sensitivity (0.1%), it has been widely applied to the characterization of semiconductor, alloy and electrode material [2]. As we know, the synthesis and many properties of materials are temperature dependent. Therefore, it is critical to realize *in situ* detection of the physical and chemical properties with temperature variations. On the other hand, the line shape changing and the energy shift of Auger spectra are customarily understood from the chemical environments while the influence of physical factors is usually neglected. In fact, the physical effects of, e.g., strain, have been proved to introduce Auger shift, and even to change the line shape [3]. Thus the thermal effect on the Auger lines is an important factor for extending AES technique into material characterizations.

GaN, possessing wide and direct energy band gap, is a promising material for the applications in short wavelength emitters, detectors, high-temperature and high-power electronics. A large amount of research has been aimed at studying both the structural and electronic properties of the GaN surface. Recently, AES technique has been employed to investigate the GaN systems. The interests were focused not only on the component concentrations but also on the strain induced Auger shifts [3-6]. Based on these pertinent results and the excellent thermal stability of GaN compound, it provides us an appropriate sample for the analysis of the Auger line shape with temperature variations.

In this work, an *in situ* thermal equipment was built in the ultrahigh vacuum chamber of AES instrument. The GaN epilayers were employed for the systematic *in situ* heating and the corresponding Auger lines were analyzed. The thermal effects on Auger line are discussed.

II. EXPERIMENTAL DETAILS

The GaN sample was grown on a sapphire substrate by metalorganic vapour phase epitaxy. A low-temperature buffer layer was first deposited and then the 10-m-thick GaN epilayers were overgrown at 1060°C. The as-grown surface was used for AES investigations. AES experiments were carried out on a Physical Electronics Model 660 (PHI-660) system with a 30° tilt angle between the sample normal and primary beam axis. The coaxial electron gun and the single pass cylindrical mirror analyzer (CMA) were used. The energy resolution of the CMA is 0.3%. The 10.0 keV electron beam with 10 nA emission current was used and the 0.1 eV step size was set in the signal collection for better energy resolution. The Auger spectra were surveyed in direct mode and the linear background substraction is adopted for high S/N ratios.

The thermal equipment consists of the heater and the temperature controller, as shown in Fig.1. The heater was set under the molybdenum sample holder and was made of a tungsten filament supported by a stainless-steel plate to provide the mechanical stability and electrical contact. Thus the holder can be heated up rapidly. Meanwhile a chromel alumel thermocouple was used for temperature detection and connected to the external temperature controller. The power supply provides 0-30 V tunable direct current (DC) and the temperature controller ensures the temperature of the sample in an accuracy of ±10 °C.

The sample was mounted on the sample holder and

*Author to whom correspondence should be addressed. E-mail: esca@jingxian.xmu.edu.cn, Tel.: +86-592-2184829, Fax: +86-592-2186129

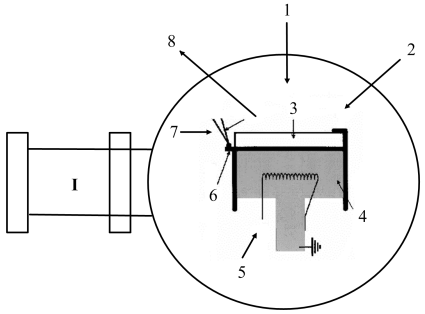

FIG. 1 Sketch of the heating module. The precision specimen stage can be installed into the vacuum system. 1: Electron gun; 2: Ion gun; 3: Sample; 4: Boron nitride insulator; 5: Tungsten filament; 6: Stainless-steel plate; 7: Chromel alumel thermocouple; 8: Detector; I: Intro chamber.

put in the intro chamber. As the vacuum therein reached the standard value, the holder was transited into the ultrahigh vacuum chamber. Under room temperature (RT), 30° tilt Ar^+ beam sputtering was carried out to clean the sample surface until the contaminants of C and O became the least. Then the required temperature and the DC voltage were set to the temperature controller, and the heating process began. When the required temperature was reached, it was automatically switched to the mode of constant temperature and the AES measurement was carried out. Generally, during heating the vacuum of the chamber will decrease gradually. In order to maintain the vacuum of the chamber not less than 5×10^{-7} Pa, the heating rate should be well set and another vacuum valve should be opened.

III. RESULTS AND DISCUSSION

The Auger spectra of the GaN surface were surveyed with *in situ* heating. The Ga LMM Auger lines at various temperatures are shown in Fig.2. The kinetic energy of Ga LMM Auger line of GaN at RT is 1066.6 eV. The curves C-G are the lines at 100, 200, 300, 400 and 500 °C, respectively. One can see that, when the sample was heated up to higher temperature, the Ga LMM Auger line shape is broadened and its peak position shifts to the lower energy side. After heated at 500 °C, the peak position downshifts as large as 0.5 eV. These phenomena indicate that the thermal effect will transform the Auger line by energy shift or shape distortion. The similar results can be observed more clearly in the Ga MVV AES spectra. Figure 3 shows the peak value of Ga MVV spectra as a function of the temperature. The peak value of Ga MVV spectrum at RT is 54.3 eV, which is consistent with that presented in Ref.[7]. The heating process also results in the negative shift for these Ga MVV lines. One can see that the peak value of Ga MVV spectra downshifts more and more distinctly with the rising temperature, and reaches 1.2 eV when heated to 500 °C. Since the transformation of the Ga MVV line is significant by heating, it is chosen for the analysis of the thermal effects on Auger lines.

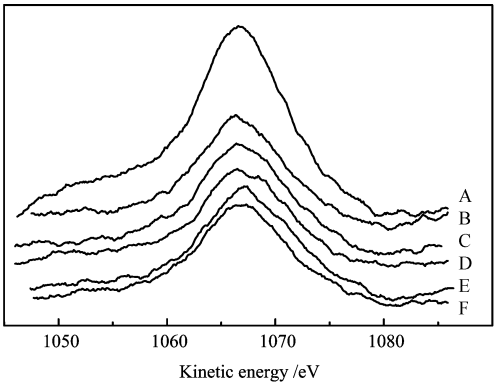

FIG. 2 Ga LMM Auger line shape of ELO GaN at various temperature. A: Room temperature, B: 100 °C, C: 200 °C, D: 300 °C, E: 400 °C, F: 500 °C.

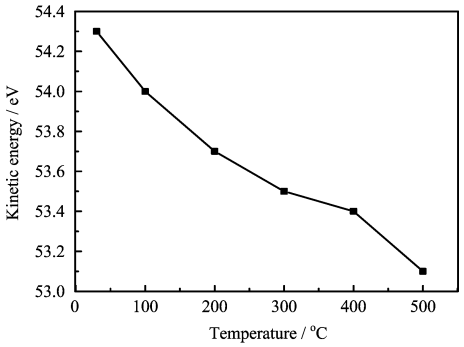

FIG. 3 The relation between kinetic energy of Ga MVV and temperature. It is found that Ga MVV decreases with heating temperature increase.

In order to understand the details of thermal effect on the Ga MVV line, we first describe the basic properties of it. The Ga MVV Auger process is an emission involved valence band, which is also be called a MVV Auger Process. The Sensitivity to the physical environment of the Ga MVV process is more explicit than that of Ga LMM process. Figure 4 shows the process of a MVV transition. The theoretical core-valence-valence (CVV) Auger integral line shape was understood as a simple linear combination of convolution of s-like and p-like local density of states (LDOS) on certain element near the surface [8]. So the theoretical MVV Auger line shape of Ga can be expressed as

$$\Gamma_{\mathrm{Ga,MVV}}(E) = C_{\mathrm{pp}}\rho_{\mathrm{p}}(E)\otimes\rho_{\mathrm{p}}(E) + C_{\mathrm{sp}}\rho_{\mathrm{s}}(E) \otimes\rho_{\mathrm{p}}(E) + C_{ss}\rho_{\mathrm{s}}(E)\otimes\rho_{\mathrm{s}}(E) \quad (1)$$

where $\rho_{\mathrm{s}}(E)$ and $\rho_{\mathrm{p}}(E)$ are the s and p partial LDOS of Ga; C_{ss}, C_{sp} and C_{pp} are the coefficients of the convolution terms.

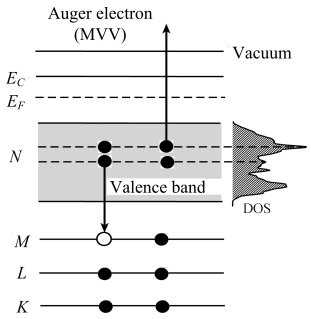

FIG. 4 Schematic diagram of MVV Auger transition. K, L and M are shell orbitals. E_F, E_C and E_V are the Fermi level, the bottom of conduction band and the energy level in valence, respectively.

The electronic structure of the valence band in the GaN surface was calculated by the first-principles method. The density-functional theory (DFT) [9,10] within the local-density approximation (LDA) and first-principles norm-conserving non-local pseudopotential method was employed. The Ceperly-Alder formula was used to form the exchange and correlation potential [11]. Local orbits were constructed from nitrogen s and p state pseudo-wave-functions. The s- and p-LDOS of Ga atoms were obtained accurately. The term of $\rho_{\rm s}\otimes\rho_{\rm s}$, $\rho_{\rm s}\otimes\rho_{\rm p}$ and $\rho_{\rm p}\otimes\rho_{\rm p}$ were calculated from the convolution integral. Figure 5 shows the fitting results of the experimental integral Auger lineshape and the theoretical curve calculation by Eq.(1) with the convolution term coefficients $C_{\rm ss}$, $C_{\rm sp}$ and $C_{\rm pp}$ of 0.00, 0.87 and 0.13, respectively. The theoretical MVV Auger line reflects the line shape of the experimental data well. The Ga MVV line is mostly contributed from the $\rho_{\rm s}\otimes\rho_{\rm p}$ term, which demonstrate the sp^3 hybridization in the Ga−N bond. Thus the peak energy and line shape is highly associated with the property of the bond and with the factors that influences it.

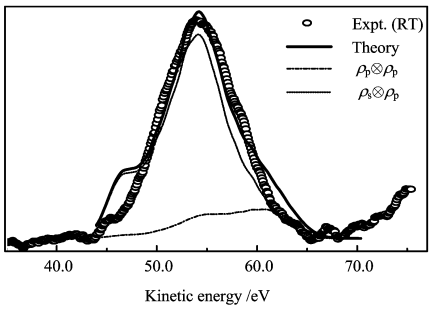

FIG. 5 Comparision of the theoretical MVV Auger peak for Ga with the experiment data from ELO GaN.

The thermal effect mainly depends on the temperature. As the temperature increases by the heating, the lattice constant of GaN increases accompanied with the thermal expansion. The lattice expansion lengthens the Ga−N bond and consequently gives rise to the redistribution of the valence electrons during the hybridization. Thus the LDOS of Ga atom will be influenced as a result. Based on Eq.(1), one can know that the convolution terms of LDOS are related with the Auger line shape. Therefore, the thermal effect would influence the Auger CVV lines via the expansion of the atomic bond and the valence electron rearrangement therein.

IV. CONCLUSIONS

In summary, an *in situ* heating system, which allows samples to be heated rapidly in ultra-high-vacuum chamber, is built for the investigation the thermal effect of Auger lines. The GaN film was studied in the temperature range of RT-500 °C. The kinetic energy of Ga LMM and MVV Auger lines were observed to shift to lower energy when heated. By using *ab initio* calculation, the theoretical Ga MVV Auger line shape was fit, which well reflects the inner property of the line. The Auger shift with heating can be explained by the valence electron rearrangement in the thermal expansion of the local bonds. Further mechanism of thermal effect on the Auger line will be carried on.

V. ACKNOWLEDGMENT

The author would like to express thanks to Professor Jun-yong Kang and Dr. Duan-jun Cai for their valuable discussions. This work was partly supported by the National Nature Science Foundation of China (No.60206030, No.10134030 and No.69976023) and the Natural Science Found of Xiamen University (No.B200337).

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