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PLD synthesis of GaN nanowires and nanodots on patterned catalyst surface for field emission study

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Abstract Patterned gallium nitride nanowires and nanodots have been grown on n-Si (100) substrates by pulsed laser deposition. The nanostructures are patterned using a physical mask, resulting in regions of nanowire growth of different densities. The field emission (FE) characteristics of the patterned gallium nitride nanowires show a turn-on field of 9.06 V/μm to achieve a current density of 0.01 mA/cm^2 and an enhanced field emission current density as high as 0.156 mA/cm^2 at an applied field of 11 V/μm. Comparing the peak FE current densities of both the nanowires and nanodots, the peak FE current density of nanowires is around 700 times higher than that of the peak FE current density of nanodots since nanodots have a lower aspect ratio compared to nanowires. The field emission results indicate that, besides density difference, crystalline quality as well as the low electron affinity of gallium nitride, high aspect ratio of gallium nitride nanostructures will greatly enhance their field emission properties.

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1 Introduction

Substrate field emission (FE) performance of continuous one-dimensional (1D) nanostructure films is often dampened by screening effects between the densely packed nanostructures. Patterning the nanostructures was observed to solve this problem and allow further FE enhancement [1]. It has been shown that nanotubes arranged in regular patterned arrays of bundles, with bundle diameter and array spacing of the order of a few microns, give much greater FE current densities than dense mat nanotubes, thin films of nanotubes, or arrayed individual nanotubes [2]. Such arrays appear ideal to be integrated into nanodevices for high-intensity electron beams from FE sources. With the recent rapid development in nanoscience and nanotechnology, patterning of field emitters is one high-potential approach for many multi-dimensional and multi-functional system applications, including patterned electron emitting displays, multi-analyte sensors, multi-channel microreactors, and microfluidic devices.

As a wide-band-gap semiconductor, gallium nitride (GaN) has attracted a lot of research attention as a material for FE devices [3]. It has strong chemical and mechanical stability and low electron affinity of 2.7–3.3 eV [4–6] and has attracted much research interest as a suitable material for new FE applications. Hence, further enhancement of FE characteristics is anticipated of 1D structures of GaN.

The FE from continuous GaN nanowire films synthesized by chemical vapor deposition (CVD), hydride vapor phase epitaxy (HVPE), and thermal evaporation has been reported [7–12]. Compared to these techniques, pulsed laser

deposition (PLD) can create a highly energetic growth precursor, leading to the formation of non-equilibrium growth conditions. PLD uses a laser beam to vaporize the target surface and create a transient, highly luminous plasma plume that expands rapidly away from the target surface. The ablated material is collected on an appropriately placed substrate upon which it condenses and where the nanowires grow. High-quality nanowires can be obtained at a fairly low substrate temperature as it is not dependent on temperature and gas flow to create species and diffuse them to the substrate as by other techniques. A relatively high deposition rate, typically hundreds of Å/min, can be achieved at moderate laser fluences, with film thickness controlled in real time by simply turning the laser on and off. Furthermore, PLD is operationally simple and cost-effective. It can be performed in a background gas or in conjunction with a source of reactive species due to the fact that a laser is used as an external energy source resulting in an extremely clean process without filaments, thus offering more flexibility than other conventional techniques [13]. In this paper, we present a direct and non-toxic way to grow patterned GaN nanowires and nanodots on n-Si (100) substrates using PLD. It was observed that chamber pressures play an important role in the structure of the synthesized products. While a N_2 chamber pressure of 26.66 Pa results in nanowire growth, a further increase of the chamber pressure to 66.66 Pa leads to the formation of nanodots instead. The nanowires' and nanodots' FE characteristics were studied and compared.

2 Experimental

The precursor material for growing GaN nanowires and nanodots was a 1-in.-diameter GaN target (99.95% purity, SCM). This target was loaded into the chamber and held by a rotating target holder for uniform ablation to avoid drilling through by the continuous irradiation of intense laser pulses. The substrates used were single-side-polished n-Si (100) substrates. They were ultrasonically cleaned using acetone, followed by IPA, and finally rinsed with de-ionized water. After evacuating the vacuum chamber to a base pressure of 6.67×10^{-5} Pa, the chamber was filled with 99.999% purified nitrogen (N_2) at a flow rate of 100 sccm. Chamber pressures of 26.66 and 66.66 Pa for the growth of nanowires and nanodots, respectively, were maintained during PLD. The growth was conducted with a KrF excimer laser (248 nm, 23 ns (full-width at half-maximum), Lambda Physik, Germany, COMPEX 102) at a laser fluence of 5.0 J/cm^2 for 15 min at a pulse repetition rate of 3 Hz. The substrates were patterned (using a transmission electron microscopy (TEM) Cu grid as a physical mask), coated with a 5 nm gold (Au) thin-film layer by an electron-beam evaporator, and placed on a substrate holder. It was positioned 3–5 cm perpendicularly opposite to the GaN target. The temperature of the substrates was kept at 700 ± 10°C during the synthesis of the nanowires. After the nanowire growth, the substrates were allowed to cool down to 100°C and below in N_2 ambient to prevent oxidation. The special feature of the PLD process is that each laser pulse ablation generates a large quantity of Ga, N, and GaN species, which is deposited onto the Au catalyst surface. The time interval between two laser pulses is 333 ms for a repetition rate of 3 Hz. This allows sufficient time for the deposited GaN species to interact with the catalyst. The morphologies of the nanowires and nanodots grown were examined using an atomic force microscope (AFM, DI 3100) and a field emission scanning electron microscope (FESEM, Hitachi S4100). The crystal structure of the nanowires was also examined with TEM (JEOL JEM-2010F with STEM option). FE measurements for the as-grown patterned GaN nanowires and nanodots were conducted in a vacuum chamber at a pressure of 8.0×10^{-5} Pa and room temperature.

3 Results and discussion

Figure 1a shows the three-dimensional (3D) AFM image of the nanowires grown at a N_2 chamber pressure of 26.66 Pa scanned across from the nanowires to the substrate region. The average step height measured is around 460 nm. Figure 1b, c show the top-view and oblique-angle FESEM images of the nanowires grown on the n-Si substrate, respectively. The GaN nanowires grown have diameters ranging from 20 to 50 nm and their lengths range from 0.5 to 1.0 µm. These nanowires also grow in an upwards direction. Figure 1d gives a low-magnification SEM image of an array of patterns formed by the nanowires grown on the patterned n-Si substrate. These patterns were defined by a TEM Cu grid as a physical mask. The size of each pattern is around 100 µm by 116 µm. The distances between each pattern of nanowires range from 37 to 45 µm. Figure 2a shows the 3D AFM image of nanodots grown at a N_2 chamber pressure of 66.66 Pa scanned across from the nanodots to the substrate region. The average step height measured is around 47 nm, nine times lower than that of the nanowires. Figure 2b shows the top-view FESEM image of the grown nanodots. The nanodots have diameters ranging from 20 to 50 nm.

The TEM images of the as-grown nanowires were obtained. Figure 3a shows the low-magnification TEM image of one of the GaN nanowires grown after ultrasonic dispersion in alcohol solution during TEM sample preparation. The diameter of the nanowire was measured to be around 10 nm. A dark spherical-like image is observed at the tip of the nanowire. This dark spherical region is the Au/Ga tip (confirmed by the energy dispersive X-ray spectrum) and is the nucleation site for the catalyzed growth of each nanowire according to the vapor–liquid–solid mechanism [14]. Figure 3b shows the corresponding high-resolution TEM image

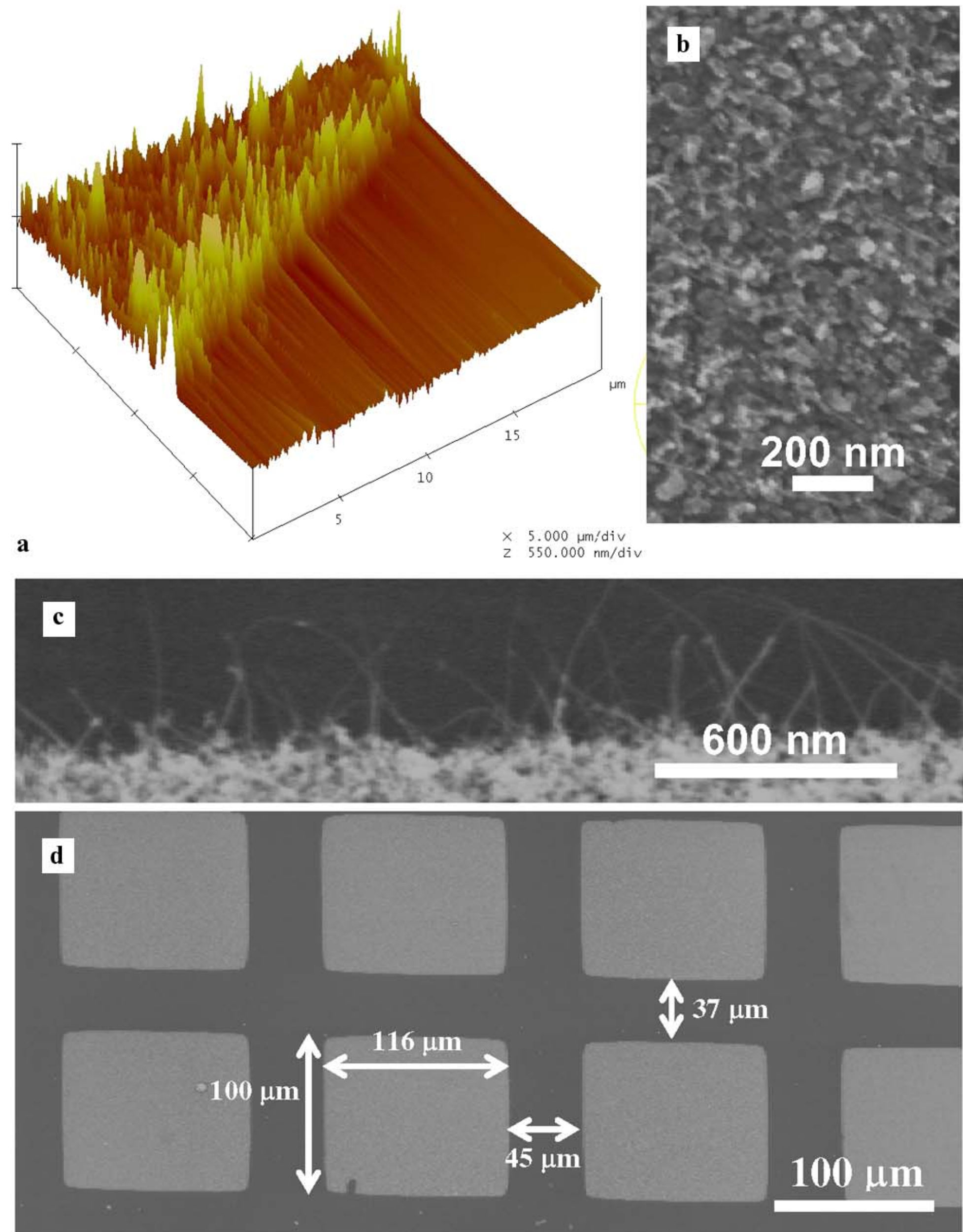

Fig. 1 (**a**) AFM 3D image scanned across from nanowires to substrate. (**b**) Top-view and (**c**) oblique-angle FESEM images of as-grown GaN nanowires. (**d**) Low-magnification SEM image of the pattern of nanowires grown on the substrate

of the nanowire with clear lattice fringes and lattice spacing of 0.28 nm for the (100) planes. It can be seen that the (100) planes, which are $\sim 60^{o}$ apart, with a d spacing of ~ 0.28 nm between the adjacent lattice fringes, present the characteristic of a hexagonal wurzite structure of the nanowire. The growth direction is perpendicular to the (010) planes. The high-resolution TEM image indicates the growth of single-crystalline GaN nanowires.

The current–voltage (I–V) characteristics of FE from these patterned GaN nanowires and nanodots were investigated. The whole FE measurement system is composed of a vacuum chamber at a low pressure of 8.0×10^{-5} Pa, using a two-parallel-plate configuration at a vacuum spacing of 100 µm, as described elsewhere [15]. A conducting indium tin oxide (ITO) glass was used as the anode. The FE current density as a function of the macroscopic electric field of the GaN nanowires is shown in Fig. 4a. The turn-on field of 9.06 V/µm was obtained based on its definition for the field to produce an emission current density of 0.01 mA/cm^2. The emission current density reached 0.16 mA/cm^2 at an applied field of 11 V/µm. This result is a tremendous improvement from that of patterned GaN nanodots grown by PLD. For patterned GaN nanodots, the FE current densities obtained (Fig. 4b) increased to a maximum of 224 nA/cm^2 at an applied field of 10.8 V/µm. Comparing the peak FE current densities of both the nanowires and the nanodots, the peak

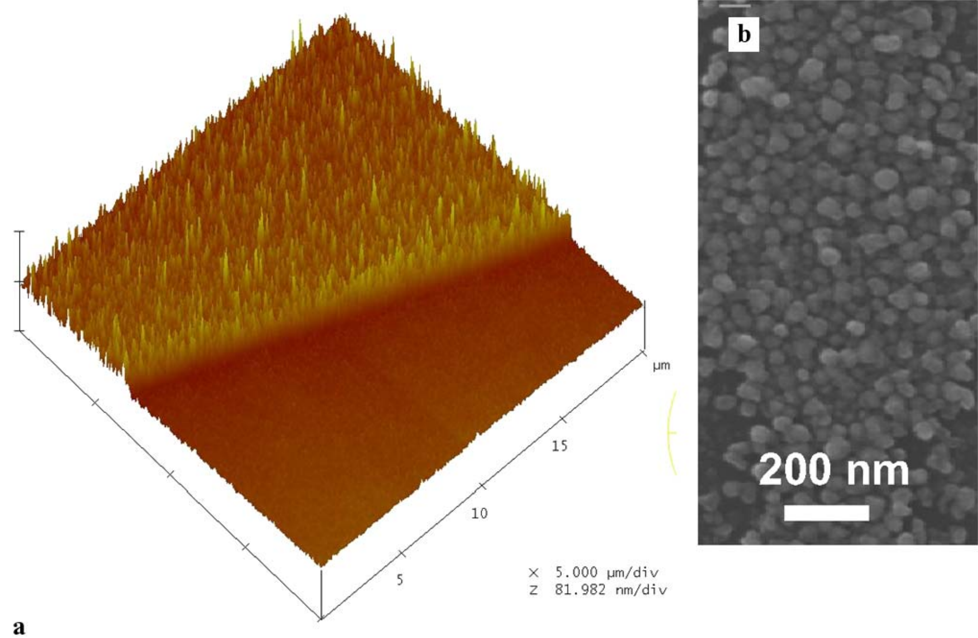

Fig. 2 (**a**) AFM 3D image scanned across from nanodots to substrate. (**b**) Top-view FESEM image of as-grown GaN nanodots

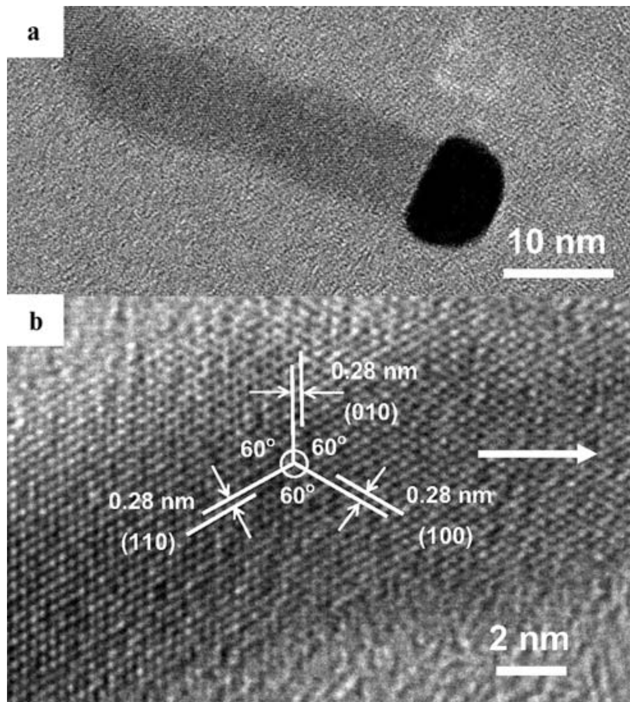

Fig. 3 (**a**) Low-magnification and (**b**) high-resolution TEM images of single GaN nanowire revealing the lattice spacing of the GaN nanowire

FE current density of nanowires is around 700 times higher than that of the peak FE current density of nanodots since nanodots have a lower aspect ratio compared to nanowires and field amplification of an emitter is determined by the radius of curvature at the tip as well as the height of the nanostructure over the substrate [16]. In addition, patterning the nanowires and nanodots reduces the screening effect caused by electrostatic screening between adjacent emitters. The electric field near the apex of the emitters increases with increasing spacing between them to an extent. Hence, patterned nanowires or nanodots have a higher and more stable emission current compared to continuous nanowire [17] or nanodot films.

The Fowler–Nordheim (F–N) plots of the patterned GaN nanowires and nanodots are shown in the insets of Fig. 4a, b, respectively. A straight-line fit of the F–N scatter plot reveals the electron emission due to F–N tunneling. From the slope of the straight line, the field enhancement factor (β) can be calculated using the F–N equation expressed as [18]

$$J = A\left(\frac{\beta^2 V^2}{\phi d^2}\right)\exp\left(-\frac{B\phi^{3/2}d}{\beta V}\right), \tag{1}$$

where J is the current density (μA/μm^2), $A = 1.4$ and $B = 6440$ are constants, ϕ is the work function (eV), d is the distance (μm) between the anode and the cathode, and V is the applied voltage (V). Assuming that the work function of GaN is 4.1 eV, the field enhancement factor β for the patterned GaN nanowires is estimated to be 350 while that for the patterned GaN nanodots is estimated to be 236. The β value reflects the degree of the FE enhancement of the tip shape on a planar surface. Due to the lower aspect ratio of nanodots compared to nanowires, the β value of the patterned nanodots is lower than the patterned nanowires. In addition, the geometry of the nanostructure, the crystal structure, and the density of emitting points also determine the value of β. Since the GaN nanowires in this study have lengths ranging from 0.5 to 1 μm, which is much shorter than other GaN nanowires reported [9, 11] (which have lengths

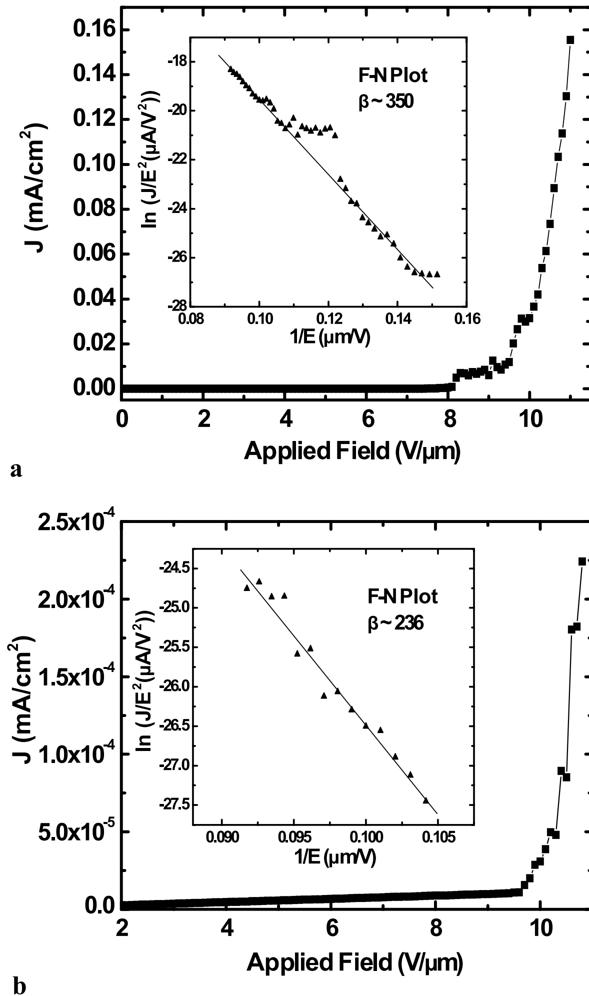

Fig. 4 FE current density of the patterned GaN (**a**) nanowires and (**b**) nanodots as a function of the applied electric field. *Insets* show their respective F–N plots

ranging from several micrometers to tens of micrometers) and shorter than the GaN nanowires reported previously by our group [17], the lower β value calculated is considered reasonable.

4 Conclusions

In summary, patterned GaN nanowires and nanodots were synthesized on n-Si substrates by PLD using the vapor–liquid–solid mechanism with Au as the catalyst. TEM grids were used as physical masks to create the patterns. The crystalline nanowire diameters ranged from 20 to 50 nm with lengths ranging from 0.5 to 1.0 μm. FE measurements showed better FE properties in these patterned GaN nanowires compared to patterned GaN nanodots grown by PLD. These patterned GaN nanowires had a turn-on field of 9.06 V/μm at a current density of 0.01 mA/cm^2 and a peak FE current density of 0.156 mA/cm^2 at an applied field of 11 V/μm. These results indicate that high aspect ratio of gallium nitride nanostructures will further enhance their FE properties, in addition to low electron affinity of GaN nanomaterials.

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References

1. H. Kind, J.M. Bonard, C. Emmenegger, L.O. Nilsson, K. Hernadi, E. Maillard-Schaller, L. Schlapbach, L. Forro, K. Kern, Adv. Mater. **11**, 1285 (1999)
2. H.M. Manohara, M.J. Bronikowski, M. Hoenk, B.D. Hunt, P.H. Siegel, J. Vac. Sci. Technol. B **23**, 157 (2005)
3. H. Yoshida, T. Urushido, H. Miyake, K. Hiramatsu, Jpn. J. Appl. Phys. **40**, L1301 (2001)
4. J.L. Shaw, H.F. Gray, K.L. Jensen, J.M. Jung, J. Vac. Sci. Technol. B **14**, 2072 (1996)
5. R.J. Nemanich, M.C. Benjamin, S.P. Bozeman, M.D. Bremser, S.W. King, B.L. Ward, R.F. Davis, B. Chen, Z. Zhang, J. Bernhole, Mater. Res. Soc. Symp. Proc. **395**, 777 (1996)
6. J.I. Pankove, H. Schade, Appl. Phys. Lett. **25**, 53 (1974)
7. B.D. Liu, Y. Bando, C.C. Tang, F.F. Xu, D. Golberg, Appl. Phys. Lett. **87**, 073106 (2005)
8. B.D. Liu, Y. Bando, C.C. Tang, F.F. Xu, J.Q. Hu, D. Golberg, J. Phys. Chem. B **109**, 17082 (2005)
9. B. Ha, S.H. Seo, J.H. Cho, C.S. Yoon, J. Yoo, G. Yi, C.Y. Park, C.J. Lee, J. Phys. Chem. B **109**, 11095 (2005)
10. H.M. Kim, T.W. Kang, K.S. Chung, J.P. Hong, W.B. Choi, Chem. Phys. Lett. **377**, 491 (2003)
11. T.Y. Kim, S.H. Lee, Y.H. Mo, H.W. Shim, K.S. Nahm, E.K. Suh, J.W. Yang, K.Y. Lim, G.S. Park, J. Cryst. Growth **257**, 97 (2003)
12. C.C. Chen, C.C. Yeh, C.H. Chen, M.Y. Yu, H.L. Liu, J.J. Wu, K.H. Chen, L.C. Chen, J.Y. Peng, Y.F. Chen, J. Am. Chem. Soc. **123**, 2791 (2001)
13. P. Merel, M. Chaker, M. Tabbal, K. Pepin, Appl. Surf. Sci. **177**, 165 (2001)
14. X. Duan, C.M. Lieber, J. Am. Chem. Soc. **122**, 188 (2000)
15. Y.W. Zhu, T. Yu, F.C. Cheong, X.J. Xu, C.T. Lim, V.B.C. Tan, J.T.L. Thong, C.H. Sow, Nanotechnology **16**, 88 (2005)
16. X.Q. Wang, M. Wang, P.M. He, Y.B. Xu, Z.H. Li, J. Appl. Phys. **96**, 6752 (2004)
17. D.K.T. Ng, M.H. Hong, L.S. Tan, Y.W. Zhu, C.H. Sow, Nanotechnology **18**, 275707 (2007)
18. J.W. Gadzuk, E.W. Plummer, Rev. Mod. Phys. **45**, 487 (1973)