Available online at www.sciencedirect.com
ScienceDirect
Journal of Solid State Chemistry 180 (2007) 2335–2339
Journal of Solid State Chemistry
www.elsevier.com/locate/jssc

Epitaxial growth of AlN films on single-crystalline Ta substrates

S. Hirata[a], K. Okamoto[b], S. Inoue[b,*], T-W. Kim[c], J. Ohta[b,1], H. Fujioka[b,1], M. Oshima[a]

[a]Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[b]Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
[c]Kanagawa Academy of Science and Technology (KAST), KSP east 301, 3-2-1, Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan

Received 14 February 2007; received in revised form 4 June 2007; accepted 5 June 2007
Available online 16 June 2007

Abstract

We have demonstrated the first epitaxial growth of AlN films on single-crystalline Ta substrates by the use of a low-temperature growth technique based on pulsed laser deposition (PLD). Although previous AlN films grown on Ta(100) and (111) substrates have exhibited quite poor crystallinity, an epitaxial AlN(0001) film with an in-plane epitaxial relationship of AlN[11$\bar{2}$0]//Ta[001] has been obtained on a Ta(110) substrate at a growth temperature of 450 °C. We found that the full-width at half-maximum values for the crystal orientation distribution in the tilt and twist directions of the AlN film were 0.37° and 0.41°, respectively. Grazing-incidence X-ray reflection (GIXR) and X-ray photoelectron spectroscopy (XPS) measurements have revealed that the AlN/Ta heterointerface is quite abrupt, and that its abruptness remains unchanged even after annealing at 1000 °C.

Keywords: Nitride semiconductor; Crystal growth; FBAR

Recently, AlN has attracted much attention because of its excellent physical properties, such as a wide direct band gap of 6.2 eV, high thermal conductivity, high breakdown electric field, and a large piezoelectric coupling coefficient. These factors make AlN suitable for a wide variety of device applications, such as film bulk acoustic resonators (FBARs) [1,2], tunneling magneto-resistance (TMR) devices [3], and short wavelength light emitters [4]. Among these applications, the FBAR device, which utilizes AlN grown on a metal electrode as a piezoelectric thin film, has been regarded as a promising candidate for a next-generation high-frequency telecommunication filter. Although polycrystalline nitride films deposited on polycrystalline metal electrodes have been used in devices of this type already [5,6], the development of single-crystalline nitride films is urgently required in order to improve device performance. It should be also noted that the abruptness of the AlN/metal heterointerfaces is inherently important in the case of high frequency filters, since the operating frequency is inversely proportional to the thickness of the AlN film. Single-crystalline AlN thin films are usually grown by metal-organic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE) at relatively high temperatures (above 800 °C) and hence it has been difficult to avoid interface reactions occurring between the AlN and the substrates. We have recently found that the use of pulsed laser deposition (PLD) allows us to dramatically reduce the substrate temperature required for epitaxial growth and to achieve atomically abrupt heterointerfaces. In fact, we have recently demonstrated that the use of PLD makes it possible to grow single-crystal group III nitride films even at room temperature [7–15] and to prepare epitaxial AlN films on single-crystalline metal substrates such as Fe, Ni, and Cu with atomically abrupt heterointerfaces [16–18]. However, the low-temperature epitaxial growth by PLD technique has never been applied to Ta substrates, which have been one of the most commonly used bottom electrodes for FBARs due to the small mismatch in thermal expansion coefficients between Ta and AlN and their low acoustic loss. In this paper, we report on the first epitaxial growth of AlN films on single-crystalline Ta substrates by PLD.

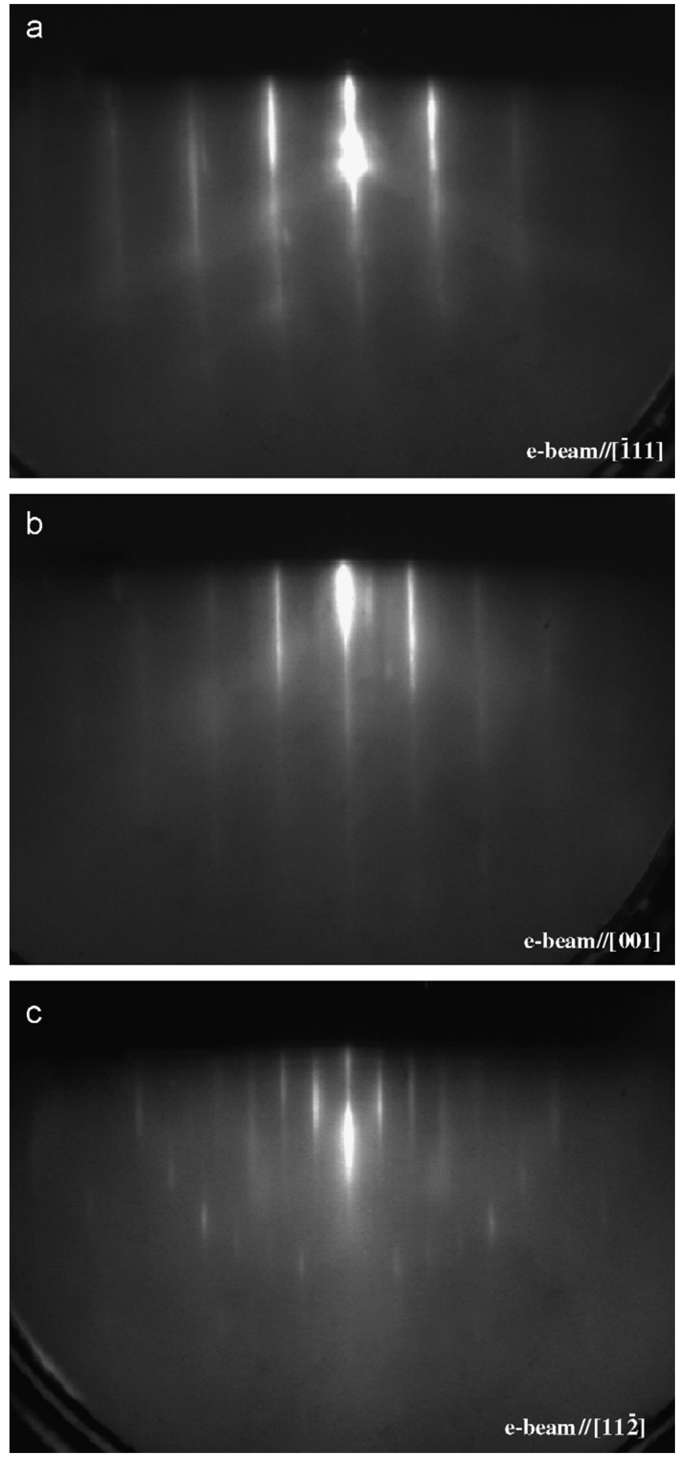
*Corresponding author. Fax: +81 3 5452 6343.
E-mail address: sinoue@iis.u-tokyo.ac.jp (S. Inoue).
[1]Also at: Kanagawa Academy of Science and Technology (KAST), KSP east 301, 3-2-1, Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan.

0022-4596/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2007.06.008

Single-crystalline Ta substrates with orientations of (110), (100), and (111) were employed as starting materials for crystal growth. The Ta substrates were flattened by chemical–mechanical polishing and then cleaned using organic solvents. After this process, the substrates were loaded into a PLD chamber with a background pressure of 5.0×10^{-10} Torr, and then annealed at various temperatures in ultra-high vacuum (UHV) for 1 h in order to obtain clean Ta surfaces. The growth of AlN films was then performed on them at a substrate temperature of 450 °C using an UHV PLD apparatus. KrF excimer laser pulses ($\lambda = 248$ nm, $\tau = 20$ ns) were used to ablate a sintered AlN target (99.99% purity) with an energy density of approximately 1–5 J/cm^2. During the growth process, N_2 gas (99.9999% purity) was introduced into the PLD chamber at a pressure of 10 mTorr. Under these growth conditions, 40 nm-thick AlN films were obtained after 5 min of growth. The structural properties of the samples were characterized by reflection high-energy electron diffraction (RHEED), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) (JEOL, JSPM 4210), electron back-scattered diffraction (EBSD) (Oxford Instruments, INCA Crystal EBSD system), high-resolution X-ray diffraction (HRXRD) (RIGAKU, ATX-G), and grazing-incidence X-ray reflection (GIXR).

Although the surfaces of Ta(110), (100), and (111) substrates just after polishing are quite smooth and AFM surface images have root-mean-square (RMS) values of approximately 0.3 nm, the RHEED images obtained from these substrates showed a halo pattern. These results indicate that the polishing process seriously damages the crystalline quality of the surface region of the Ta substrates. Therefore we performed a UHV annealing process in order to restore their crystallinity. Figs. 1(a)–(c), respectively, show RHHED images for Ta(110), (100), and (111) substrates annealed at 1100 °C for 1 h. One can see that all of the images exhibit sharp streaks and the (100) and (111) surfaces also show reconstructed patterns. The surface morphology of the Ta substrates is also improved by the annealing. The RMS values for the surface roughness were estimated to be less than 0.2 nm. These results indicate that flat Ta surfaces that are suitable for epitaxial growth were obtained by annealing at 1100 °C for 1 h under UHV conditions.

Fig. 2 shows C1*s* XPS spectra for the surface of a Ta(110) substrate during UHV annealing at various temperatures. Although a peak for C1*s* can be clearly seen in the spectrum of the as-polished substrate, the peak intensity was significantly decreased by annealing at 400 °C. One can see that a new peak at a binding energy of 283 eV appears after annealing at 500 °C. This new peak is presumably attributed to segregation of carbon impurities from inside the substrate onto the surface during the annealing process. However, this peak also disappears after annealing at 700 °C. We have also found that the peaks for the native oxide of Ta in the Ta 4*f* XPS spectra disappear after annealing at 500 °C. These results suggest that surface



Figs. 1. RHEED patterns for: (a) (110), (b) (100), and (c) (111) Ta substrates annealed at 1100 °C for 1 h.

contaminants are effectively removed and that the crystallinity of the surfaces is restored by annealing under UHV conditions at 1100 °C.

Figs. 3(a)–(c), respectively, show RHEED patterns for AlN films grown on Ta(110), (100), and (111) substrates at a substrate temperature of 450 °C. Basically, all of the RHEED patterns are for the AlN (0001) plane and we have observed clear AlN 0 0 0 2 diffraction peaks for the AlN

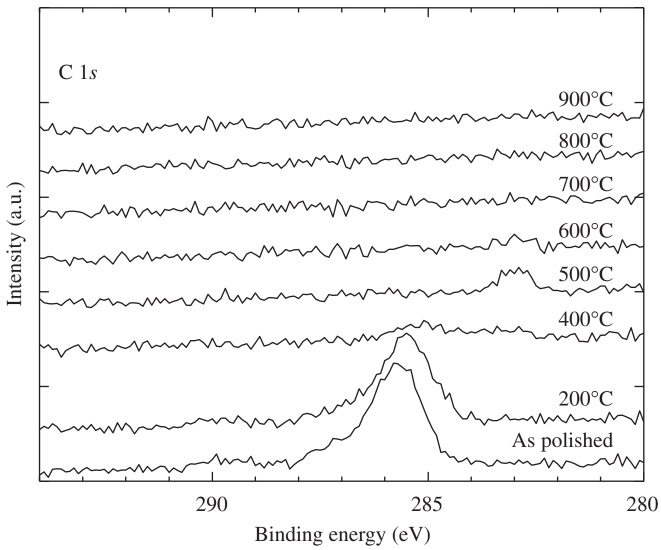
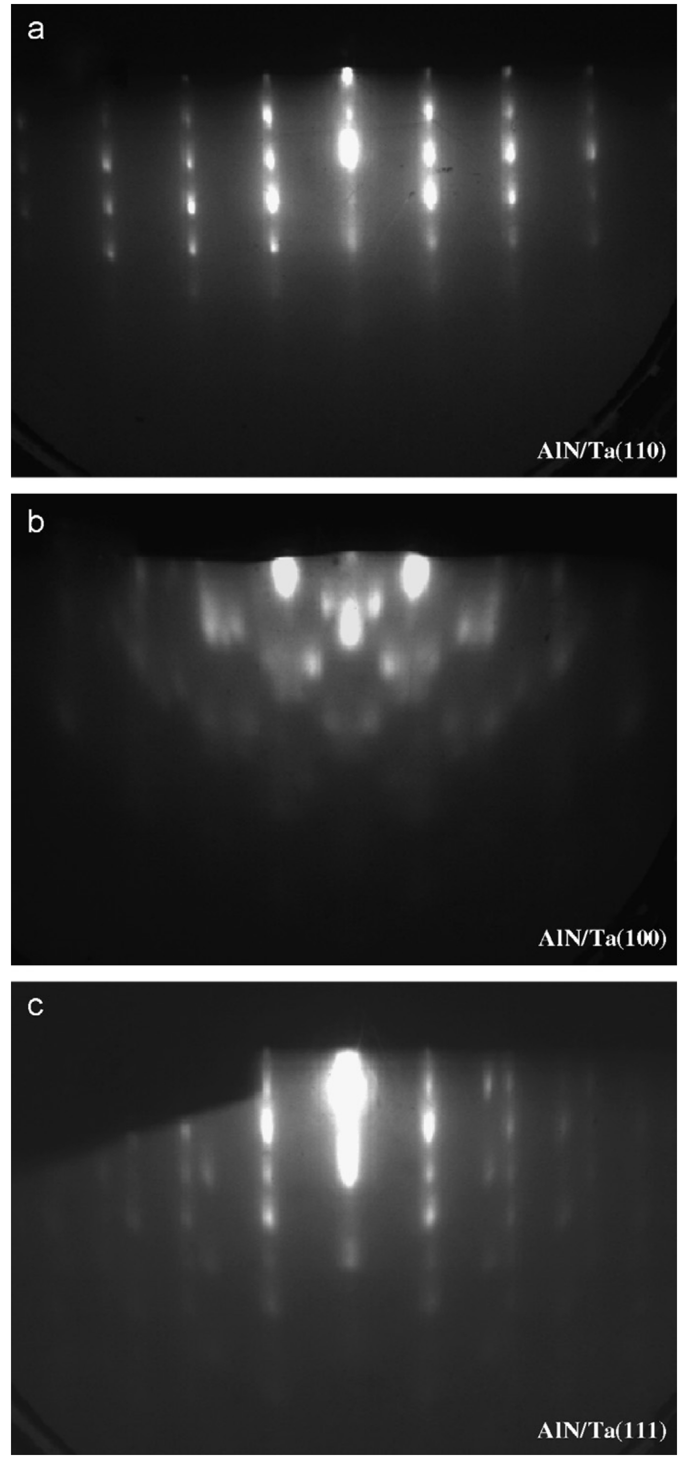


Fig. 2. C1s XPS spectra for a Ta(110) surface annealed at various temperatures.

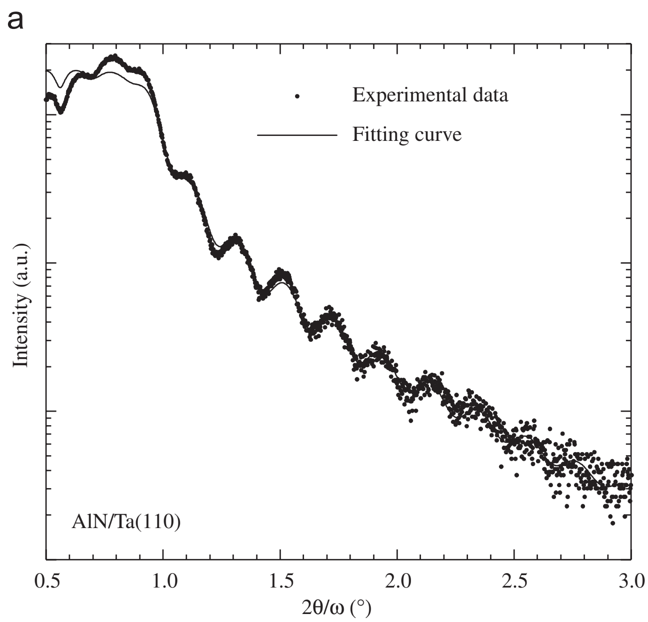
films in the symmetrical $2\theta/\omega$ scans of HRXRD measurements. We have found that the pattern for AlN grown on Ta(100) exhibits the same pattern for every 30° of in-plane substrate rotation in spite of its hexagonal structure, indicating that the AlN film contains 30° in-plane domains. This phenomenon is quite reasonable because the Ta(100) plane has four-fold rotational symmetry, while the AlN(0001) plane has six-fold rotational symmetry. We have also found that the RHEED pattern for AlN grown on Ta(111) contains faint arcs, indicating that the film quality is quite poor in spite of the symmetrical similarity between AlN (0001) and Ta(111). We temporarily ascribe this phenomenon to the high reactivity of the (111) plane of bcc materials [19]. On the other hand, the RHEED image for the AlN film grown on a Ta(110) substrate shows a sharp, spotty pattern, which suggests that an epitaxial AlN film has been successfully grown on the Ta(110) substrate. Careful interpretation of the RHEED patterns before and after growth of the AlN film led us to conclude that an epitaxial AlN film had grown on the Ta(110) substrate with in-plane alignments of AlN[$11\bar{2}0$]//Ta[001]. This successful epitaxial growth of AlN(0001) on Ta(110) is probably attributed to the relatively small lattice mismatch of 5.4% along AlN[$11\bar{2}0$] and Ta[001] [20].

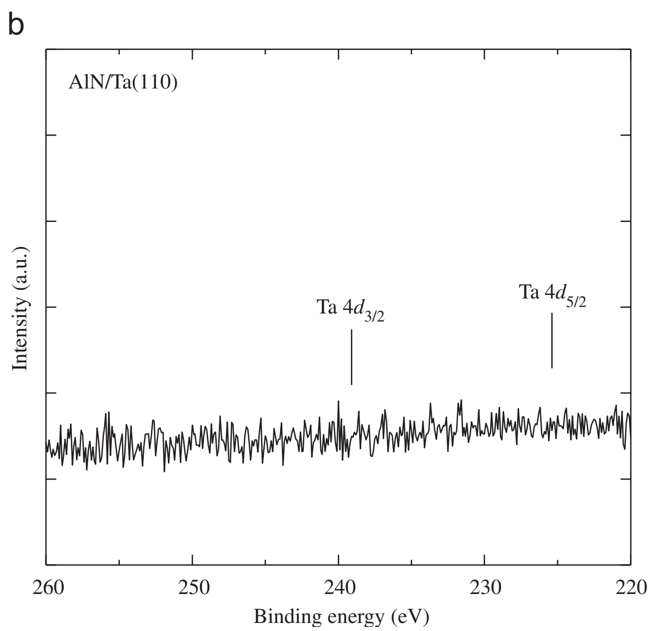
We investigated the crystalline quality of an AlN layer grown on Ta(110) by checking the distributions of the [0001] and [$10\bar{1}0$] pole figures using EBSD. The full-width-at-half-maximum (FWHM) values of the crystalline distribution in the tilt and twist directions for AlN grown at 450 °C are 0.37° and 0.41°, respectively. These values are in the same range as the best values obtained for AlN grown on other metallic substrates [17]. In the phi-scan for AlN $1 0 \bar{1} 0$ in HRXRD measurements, we observed the clear six-fold symmetry, which indicates the growth of the single-domain AlN film.



Figs. 3. RHEED patterns for AlN films grown on: (a) Ta(110), (b) Ta(100), and (c) Ta(111) with an incident electron beam along the AlN[$11\bar{2}0$] direction.

Since Ta substrates are much more reactive than the conventional oxide substrates that are used for group III-nitrides, the structural properties of the AlN/Ta hetero-interfaces were investigated in detail by GIXR. The thickness of the interfacial layer can be obtained by fitting the GIXR curve with the Fresnel equation [21,22].





Figs. 4. (a) GIXR data and fitting curve for an AlN/Ta(110) structure. (b) Ta 4*d* XPS spectrum for the AlN surface.

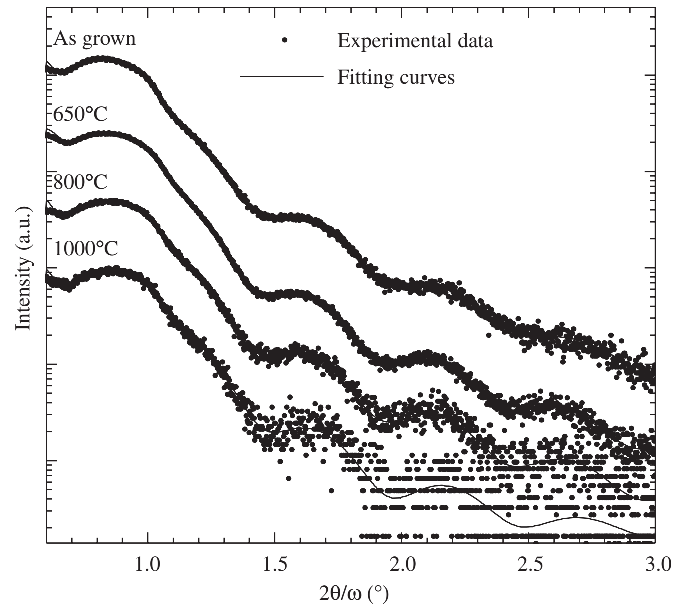


Fig. 5. Annealing-temperature dependence of GIXR curves for the AlN/Ta(110) structure.

Fig. 4(a) shows the GIXR data and the simulated curves for 40-nm-thick AlN films grown on Ta(110) at 450 °C. One can see that the simulated curves fit the experimental data quite well. The estimated interfacial layer thickness is less than 1 nm for all of the substrates. XPS measurements of the AlN surfaces were also performed in order to check that the possible out-diffusion of Ta atoms from the substrate onto the film surface was suppressed. Fig. 4(b) shows Ta 4*d* XPS spectra for the surfaces of AlN films grown on Ta(110) substrates. Neither Ta $4d_{3/2}$ peaks at 238 eV nor $4d_{5/2}$ peaks at 226 eV are seen in the spectra. These results indicate that interface reactions between AlN and the Ta substrates are not significant at this temperature, and that the heterointerfaces are abrupt.

To investigate the thermal stability of heterointerfaces between AlN and Ta, we have performed UHV annealing on a 16-nm-thick AlN films. Fig. 5 shows the changes in the GIXR curves after UHV annealing at 650, 800, and 1000 °C for 10 min. The difference in the intensity of the GIXR curves is attributed to the setting of the measurement, such as the size of collimation slits, which has no influence on the shape of GIXR curves. One can see that the shapes of the curves do not exhibit any clear changes. In fact, the estimated interfacial layer thickness remains unchanged by the annealing. These results indicate that the AlN/Ta heterointerface is quite stable with respect to high temperatures (up to 1000 °C), which is important for device fabrication.

Ta substrates with clean, flat surfaces have been obtained by polishing and UHV annealing. Although AlN films grown on Ta(100) and (111) substrates have exhibited quite poor crystallinity, an epitaxial AlN(0001) film with an in-plane epitaxial relationship of AlN[11$\bar{2}$0]//Ta[001] has been obtained for the first time on a Ta(110) substrate by the use of a PLD low-temperature growth technique. We have found that the FWHM values for the crystal orientation distribution in the tilt and twist directions of the AlN film are 0.37° and 0.41°, respectively. GIXR and XPS measurements have revealed that the AlN/Ta heterointerface is quite abrupt and its abruptness remains unchanged even after annealing at 1000 °C. These results indicate that the PLD low temperature growth technique is a promising route for improving the performance of nitride devices such as FBARs on metal substrates.

References

[1] K.M. Lakin, J.S. Wang, Appl. Phys. Lett. 38 (1981) 125.
[2] S.H. Lee, K.H. Yoon, J.K. Lee, J. Appl. Phys. 92 (2002) 4062.
[3] G.A. Prinz, Science 282 (1998) 1660.
[4] Y. Taniyasu, M. Kasu, T. Makimoto, Nature 441 (2006) 325.
[5] J.B. Lee, J.P. Jung, M.H. Lee, J.S. Park, Thin Solid Films 447/448 (2004) 610.
[6] K. Yamada, H. Asahi, H. Tampo, Y. Imanishi, K. Ohnishi, K. Asami, Appl. Phys. Lett. 78 (2001) 2849.
[7] J. Ohta, H. Fujioka, M. Oshima, K. Fujiwara, A. Ishii, Appl. Phys. Lett. 83 (2003) 3075.
[8] A. Kobayashi, J. Ohta, H. Fujioka, K. Fujiwara, A. Ishii, Appl. Phys. Lett. 88 (2006) 181907.
[9] J. Ohta, H. Fujioka, M. Oshima, Appl. Phys. Lett. 83 (2003) 3060.
[10] J. Ohta, H. Fujioka, S. Ito, M. Oshima, Appl. Phys. Lett. 81 (2002) 2373.
[11] A. Kobayashi, H. Fujioka, J. Ohta, M. Oshima, Jpn. J. Appl. Phys. 43 (2004) L53.
[12] Y. Kawaguchi, J. Ohta, A. Kobayashi, H. Fujioka, Appl. Phys. Lett. 87 (2005) 221907.
[13] G. Li, J. Ohta, A. Kobayashi, H. Fujioka, Appl. Phys. Lett. 89 (2006) 182104.
[14] M.-H. Kim, M. Oshima, H. Kinoshita, Y. Shirakura, K. Miyayama, J. Ohta, A. Kobayashi, H. Fujioka, Appl. Phys. Lett. 89 (2006) 031916.
[15] A. Kobayashi, Y. Kawaguchi, J. Ohta, H. Fujioka, Appl. Phys. Lett. 89 (2006) 111918.
[16] T.-W. Kim, N. Matsuki, J. Ohta, H. Fujioka, Appl. Phys. Lett. 88 (2006) 121916.
[17] K. Okamoto, S. Inoue, N. Matsuki, T.-W. Kim, H. Fujioka, M. Oshima, Phys. Status Solidi (a) 202 (2005) R149.
[18] S. Inoue, K. Okamoto, N. Matsuki, T.W. Kim, H. Fujioka, Appl. Phys. Lett. 88 (2006) 261910.
[19] M.J.S. Spencer, A. Hung, I.K. Snook, I. Yarovsky, Surf. Sci. 513 (2002) 389.
[20] J. Narayan, B.C. Jain, J. Appl. Phys. 93 (2003) 278.
[21] L.G. Parratt, Phys. Rev. 95 (1954) 359.
[22] L. Nevot, P. Croce, Rev. Phys. Appl. 15 (1980) 761.