

The effect of growth parameters on CrN thin films grown by molecular beam epitaxy

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Abstract

In this paper, we report on the controlling of the effect of growth parameters such as substrate temperature and the ratio of Cr and N atoms on phase formation, surface morphology and crystallization of CrN(001) thin films grown by plasma-assisted molecular beam epitaxy on the MgO(001) substrate. The reflected high energy electron diffraction, atomic force microscopy, X-ray diffraction and scanning tunneling microscopy are used to characterize the thin films grown under various conditions. High-quality CrN(001) thin films are achieved at a substrate temperature 430 °C with a low Cr deposition rate.

Keywords: A. Chromium nitride B. Crystalline orientation C. Molecular beam epitaxy D. Scanning tunneling microscopy E. Reflection high energy diffraction F. X-ray diffraction

1. Introduction

CrN has attracted much attention in last two decades not only because of its high mechanical hardness and good corrosion resistance, but also because of its intriguing magnetic and electronic properties. For example, CrN is paramagnetic at room temperature and with the lowering of the temperature, an anti-ferromagnetic phase appears at 260-286 K, depending on the atom ratio of Cr and N, which has been accepted by most groups [1, 2].

The electronic transport properties were extensively investigated on CrN samples in the forms of compressed poly-crystalline pellets [1], poly-crystalline films [2] and single-crystal films [3] grown by solid-state sintering, sputtering technique, pulsed laser deposition [4] and molecular beam epitaxy (MBE) [5, 6]. However, the controversy still remains on its

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electronic properties, which is likely due to the different micro-structures and compositions present in the samples prepared by different groups [3, 5].

It is well known that the micro-structure and composition of the thin film strongly depend on the growth parameters. By carefully tuning them, the high-quality thin film with low roughness and desired micro-structure can be achieved, which plays key roles in the development of modern semiconductor industry related to microelectronic devices. Moreover, the optical, electronic and mechanical properties of the thin film are inevitably affected by its surface morphology and composition. Here, for CrN thin film, in the same way, its application in electronics and coatings due to its high hardness are also constrained by its micro-structure and composition, which requires knowing well how the growth conditions affect the morphology and microstructure. Gall *et al.* [7, 8] investigated the effect of growth parameters on the surface morphology and the microstructure of single-crystal CrN thin films by sputtering technique. For MBE technique, however, the reports are few regarding the effect of growth parameters on the phase formation and surface morphology, though the single crystal CrN thin films have been achieved [5, 6].

In this paper, we use reflection high energy electron diffraction (RHEED), X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning tunneling microscopy (STM) to characterize CrN(001) thin films and try to systematically understand how the growth temperature and rate affect the crystallization and surface morphology of CrN(001) thin films grown by plasma-assisted MBE.

2. Experimental details

The CrN(001) thin film is grown on the MgO(001) substrate in a custom-designed MBE growth system installed with Cr effusion cell and N₂ plasma source with high-purity N₂ (99.999%) as a gas source. The base pressure in MBE growth chamber is 2.7×10^{-8} Pa ($\sim 2 \times 10^{-10}$ Torr). During the growth, the power of N₂ plasma source is set to 500 W and the pressure of growth chamber is kept at 1.3×10^{-3} Pa (1.1×10^{-5} Torr). RHEED is used to monitor the whole growth process *in situ* for ease of adjusting the growth parameters in real time. Once the growth is finished, the sample is cooled down to a lower temperature (<100 °C) and then transferred to the analysis chamber with the vacuum better than 8×10^{-9} Pa (6×10^{-11} Torr), where the STM measurements are carried out *in situ*. The AFM system, manufactured by Park Scientific Instruments company with model Autoprobe CP, is used to investigate the morphology of thin films *ex situ* in contact mode under ambient conditions. The AFM tip is made of silicon nitride and has a resonant frequency about 30 kHz and a force constant of 0.27 N/m. For XRD measurements, the copper target is used as the X-ray source and XRD data are measured in traditional θ - 2θ scan and ω -scan modes (ω : an angle between incident beam and the sample surface) under ambient conditions. The former is helpful to get the information regarding the phase formation while the latter is rather useful for the evaluation of the crystallinity of the epitaxial thin film.

In order to obtain systematic information regarding the effect of growth parameters on the properties of CrN(001) films, the various substrate temperatures and flux ratios of N/Cr (J_N/J_{Cr}) are adopted to grow samples. The general procedure is as follows. First, the

MgO(001) substrate is chemically cleaned using acetone and isopropanol before being put into the load-lock chamber connecting with main analysis and growth chambers. Second, the MgO(001) substrate is heated up to 1000 °C, at which it is annealed for ~ 1 hour with N₂ plasma on until the streaky RHEED pattern is achieved. Third, the substrate is cooled down to an appropriate temperature, at which the growth is commenced with the N₂ plasma on and the shutter of Cr effusion cell open. The stopping and starting of the growth are controlled by closing and opening the shutter of Cr effusion cell, respectively.

The flux of Cr, J_{Cr} , is measured by a quartz crystal microbalance. The flux of N₂ plasma, J_N , is calibrated by the growth of single-crystal GaN(0001) thin film without any reconstruction, which was reported previously [9]. Here, a brief description is given below. The GaN(0001) is homo-epitaxially grown on GaN that was grown on (0001)sapphire by metal organic chemical vapor deposition. It is worth pointing out that the careful adjustment of Ga flux by monitoring the variation of the RHEED pattern is the key to achieving GaN(0001) without reconstruction. In the Ga-rich regime, RHEED pattern is streaky; then the Ga flux is gradually reduced and at a transition point the RHEED pattern is brightening; further decreasing Ga flux causes the presence of a spotty RHEED pattern, meaning that the growth is in the N-rich regime. The J_N is equal to the Ga flux corresponding to the transition point, $2.29 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, which is kept constant for different growth runs by unchanging N₂ pressure in the growth chamber.

3. Results and discussion

3.1. Real-time RHEED results

RHEED is a powerful tool for monitoring the growth process of the thin film *in situ*. Observing the variation of the RHEED pattern in real time during growth is helpful to adjust and further optimize the growth parameters with the goal of yielding high-quality thin films. In this paper, we carefully made comparisons between the CrN(001) thin films grown at different temperatures with various Cr fluxes. As mentioned above, the flux of N₂ is kept constant for the growth of different thin films by keeping the pressure in the MBE growth chamber unchanged. Accordingly, changing J_{Cr} results in a change in the ratio J_N/J_{Cr} , which theoretically varies the chemical composition in the sample. In general, the growth rate is controlled by the impinging rate of Cr atoms on the surface of substrate, which is inversely proportional to the flux ratio J_N/J_{Cr} since J_N is unaltered.

Figure 1 shows the RHEED patterns taken during the growth of three samples. Shown in Panel I is the evolution of RHEED patterns with the growth time for sample A grown at a substrate temperature ~ 220 °C with the flux ratio $J_N/J_{Cr}=3/2$. Before growth, it could be seen that the RHEED pattern for MgO(001) substrate shows sharp streaks [Panel I(a)], implying that the surface of MgO(001) substrate is smooth and suitable for epitaxial growth. Opening the shutter of Cr effusion cell for 2 min makes the RHEED pattern hazy while sharp streaks change into spotty ones [Panel I(b)]. Here, “spotty” means that the RHEED pattern exhibits disconnected streaks. Five minutes later, the streaks become indistinct [Panel I(c)], suggesting that the surface of MgO(001) substrate is completely buried by the randomly distributed Cr atoms. This may be due to the mismatch between the high deposition rate

and the very low surface mobility of Cr atoms impinging on the MgO(001) substrate at such a low growth temperature. Accordingly, the already existing Cr atoms on the substrate surface are susceptible to be “pinned” by the subsequently arriving Cr atoms at the positions where they land before they find the sites suitable for the epitaxial growth [10]. In other words, the Cr atoms tend to pile up, resulting in the kinetic instabilities [11] and finally leads to the formation of a polycrystal sample manifesting itself as a ring-like RHEED pattern [see Panel I (d)]. Even if it is annealed for some time at 650 °C, no change is observed [see Panel I(e)].

In order to understand better how the surface mobility of Cr atoms affects the epitaxial growth of CrN(001) thin film, sample B is initially grown at a higher temperature (430 °C) with the same J_{Cr} as that used for sample A. The evolution of RHEED pattern with growth time for sample B is shown in Panel II of Fig. 1. Shown in Panel II(a) is the RHEED pattern of the post-annealed MgO(001) substrate taken along [110] direction, where the sharp streaks similarly suggest that a smooth surface is obtained. Five-minute opening of Cr effusion cell results in a spotty RHEED pattern but the traces of the streaks are still distinguishable [see Panel II(b)], which is different from sample A grown at 220 °C [Panel I(b)]. The reason may be that the high substrate temperature enhances the surface diffusion of Cr atoms, which is favorable to prevent the accumulation of Cr atoms at their landing sites. At this stage, the shadowing effect originating from lower impinging rate of Cr atoms for a given site than other sites may play a role in roughening the surface. So the RHEED pattern looks slightly spotty. Twenty minutes later, extra spots appear on the RHEED pattern [Panel II(c)], suggesting the presence of impurity phases or the mis-orientation of the CrN grains. Subsequent growth at 650 °C confirms that these extra spots mainly result from the mis-orientation of grains, which causes the tilting of the streaks in the RHEED patterns shown in Panel II(d) and (e) corresponding to the 30-second and 40-minute growth at 650 °C, respectively.

To prevent the mis-orientation of grains during growth, the J_N/J_{Cr} is increased for sample C to 10. As mentioned above, in our case the flux of N₂ plasma is kept unaltered. So increasing J_N/J_{Cr} also means decreasing J_{Cr} and in turn the deposition rate of Cr atoms on the substrate surface. The RHEED patterns shown in Panel III of Fig. 1 correspond to the evolution of RHEED pattern with the growth time for sample C grown at a temperature 430 °C with $J_N/J_{Cr}=10$. Panel III(a) shows the RHEED pattern of the MgO(001) substrate along [110] direction with a smooth surface just before growth. Even from the beginning to the ending of the growth, all the RHEED patterns exhibit sharp streaks, suggesting that the epitaxial growth indeed takes place [see Panel III(b)-(e)]. It is worth noting that after growing 23-nm-thick CrN(001), three extra spots appear on the RHEED pattern [Panel III(c)], which almost fade away after annealing the sample at 650 °C for half an hour, followed by the growth of 12-nm-thick CrN(001) thin film [Panel III(e)] at 430 °C. This phenomenon is similar to that reported in our previous paper [5].

Above results suggest that the low J_{Cr} and a substrate temperature around 430 °C are favorable for the growth of epitaxial CrN(001) thin film. We attempt to speculate that the extra spots appearing on the RHEED patterns of sample C may be due to the slightly lower J_{Cr} . To confirm this conjecture, we tried to grow sample D at 430 °C with the higher J_{Cr}

($J_N/J_{Cr}=6.5$). The RHEED results are shown in Fig. 2, where (a) and (b) are RHEED patterns taken along [110] and [100] directions of the MgO(001) substrate, respectively, while figures (c) and (d) correspond to the RHEED patterns of CrN(001) taken along two corresponding directions. Moreover, the RHEED patterns in Fig. 2(c) and (d) exhibit sharp streaks, suggesting that the atomically flat CrN(001) thin film is achieved. Note that during growth no extra spots appear on the RHEED patterns. This result suggests again that the low J_{Cr} and 430 °C are favorable for the epitaxial growth of CrN(001) thin film on the MgO(001) substrate.

3.2. Surface morphology studies

Some samples mentioned above are selected to perform AFM measurements in the contact mode with silicon nitride tip to explore the effect of growth parameters on the surface morphology. AFM results reveal that the surface morphology varies when the growth temperature and flux ratio J_N/J_{Cr} are adjusted, as shown in Fig. 3. As mentioned above, the sample A in the poly-crystalline form is grown at a low substrate temperature (220 °C) with the high Cr deposition rate ($J_N/J_{Cr}=3/2$). The feature of its surface is dominated by huge ridges [see Fig. 3(a)]. We attempt to attribute this phenomenon to the low surface mobility of Cr atoms when the substrate temperature is too low. This causes the growth instabilities since MBE growth process of CrN(001) thin film involves the competition between Cr deposition process intending to make the system non-equilibrium, and the diffusion process intending to equilibrate the system [11, 12]. The Cr atoms landing on the substrate are riveted at the landing positions by subsequently arriving Cr atoms [10] before they move to the sites suitable for the epitaxial growth. Thus, a high J_{Cr} and a low growth temperature easily lead to the huge-ridge morphology.

For sample B grown at a higher temperature 430 °C with the same J_{Cr} as that used for sample A, the epitaxial growth develops but the terrace is tilted relative to the normal of substrate by 70°, which can be clearly seen from the enlarged version of the marked rectangular frame in the inset of Fig. 3(b). This is consistent with 20° tilting of the streaks in RHEED pattern of CrN film with respect to those of MgO(001) substrate [see Panel II(d) and (e) of Fig. 1]. The tilting may be because in this situation (high deposition rate) the CrN prefers to grow along the edges of the already existing islands [10].

As aforementioned, the RHEED patterns of sample C grown at 430 °C with $J_N/J_{Cr}=10$ exhibit sharp streaks. For this epitaxially grown sample, AFM measurements indicate that the surface is dominated by the uniformly distributed mounds, as shown in Fig. 3(c), similar to the CrN sample grown by sputtering technique [7]. The roughness is low (R.M.S. roughness ~ 1.0 nm), suggesting that the low J_{Cr} is indeed favorable for the epitaxial growth of the flat CrN(001) thin film.

The STM is employed to investigate the surface morphology of sample D grown at 430 °C with $J_N/J_{Cr}=6.5$ whose RHEED patterns are shown in Figs. 2(c) and (d). Fig. 4(a) shows a topographic STM image taken in a large area (120×120 nm²). It could be seen that the whole surface consists of mounds with height less than 1 nm, demonstrating a smooth surface. If this sample has good crystallization, the STM image with the atomic resolution should be acquired with a sharp STM tip. As is expected, the atomically resolved

Table 1: This table summarizes the Cr flux (J_{Cr}), initial growth temperature (T_g), annealing temperature (T_a), morphology, crystallization and thickness of four CrN(001) thin films grown on MgO(001) mentioned in the text. “No” in the column of T_a means that the sample has never been annealed.

sample	J_{Cr} ($\text{cm}^{-2}\text{s}^{-1}$)	T_g ($^{\circ}\text{C}$)	T_a ($^{\circ}\text{C}$)	morphology	crystallization	thickness
A	1.53×10^{14}	220	650	huge ridge	polycrystal	89 nm
B	1.53×10^{14}	430	No	tilting terrace	misorientation	91 nm
C	2.29×10^{13}	430	650	regular mound	high quality	35 nm
D	3.52×10^{13}	430	No	regular mound	high quality	37 nm

topographic STM image is achieved. One part of a typical STM image is shown in Fig. 4(b). This atomic-resolution image suggests the high-quality crystallization of the CrN(001) thin film grown at 430 $^{\circ}\text{C}$.

3.3. XRD analysis

The XRD measurements are performed on samples C and D at ambient conditions to identify the phase constituents and analyze the crystallinity for CrN(001) films. The typical XRD results obtained on sample C are shown in Fig. 5. Figure 5(a) shows the traditional θ - 2θ scan with 2θ ranging from 42.0° to 44.5° , where one could find that the CrN(002) peak corresponding to $\text{CuK}\alpha_1$ is at 43.48° . The simple calculation yields the *out-of-plane* lattice constant $a_{\perp} \simeq 4.16 \text{ \AA}$. The *in-plane* lattice constant a_{\parallel} obtained from RHEED measurements is about 4.14 \AA . Although these values are consistent with previous data reported by our group [5] and other groups [1, 3, 7], the a_{\parallel} is smaller than a_{\perp} , resulting in the deviation from an ideal cubic crystal structure. This may be caused by the compressive strain effect for very thin films, as pointed out in our previous paper [5]. It should be mentioned that the CrN(001) thin film contains no other impurity phases, which is verified by the XRD measurements with a wide 2θ range from 30° to 140° , not shown here.

Plotted in Fig. 5(b) are the measured rocking curve and the corresponding Lorentzian fit that produces a full width at half maximum (FWHM) $\Gamma_{\omega}=0.24^{\circ}$. This value is smaller than 0.6° reported by Ney et al. [6] but slightly larger than that we previously reported (0.1°) [5]. Since the thickness (35 nm) of our sample is almost the same as that in Ref. [6] and much thinner than that (149 nm) we previously reported, the crystalline quality of the present sample could be comparable to that of our previous sample. For sample D, the rocking curve results indicate that FWHM is slightly larger (0.32°) although both samples C and D have almost the same thickness. As mentioned above, sample C is annealed at 650°C while sample D is not. This may suggest the possibility that the high-temperature annealing is helpful to improve the crystallization of sample C.

In order to see more clearly the effect of growth parameters on the crystallization of CrN(001) thin films, we summarize the main results mentioned above in Table 1. Note that during different growth runs the flux of N_2 , $J_N=2.29 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, is kept unaltered.

4. Conclusion

To summarize, the Cr flux and the initial growth temperature have a strong effect on the surface morphology and crystallinity of CrN(001) thin films grown on MgO(001) substrate. High Cr flux and too low substrate temperature result in a polycrystal with the surface dominated by “huge ridges”. By carefully tuning the growth parameters including deposition rate of Cr atom and the substrate temperature, the high-quality CrN(001) thin films are achieved at a substrate temperature 430 °C with the low Cr flux. The detailed measurements and analysis of electronic structure (scanning tunneling spectroscopy measurement), resistivity, chemical composition and magnetism on such samples are being conducted in order to clarify the intrinsic electronic properties of CrN(001) thin films.

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References

- [1] J. D. Browne, P. R. Liddell, R. Street, and T. Mills, *Phys. Status Solidi A* 1 (1970) 715.
- [2] Y. Tsuchiya, K. Kosuge, Y. Ikeda, T. Shigematsu, S. Yamaguchi, and N. Nakayama, *Mater. Trans., JIM* 37 (1996) 121.
- [3] D. Gall, C. S. Shin, R. T. Haasch, I. Petrov, and J. E. Greene, *J. Appl. Phys.* 91 (2002) 5882.
- [4] K. Inumaru, K. Koyama, N. Imo-oka, and S. Yamanaka, *Phys. Rev. B* 75 (2007) 054416.
- [5] C. Constantin, M. B. Haider, D. Ingram, and A. R. Smith, *Appl. Phys. Lett.* 85 (2004) 6371.
- [6] A. Ney, R. Rajaram, S. S. P. Parkin, T. Kammermeier, and S. Dhar, *Appl. Phys. Lett.* 89 (2006) 112504.
- [7] D. Gall, C.-S. Shin, T. Spila, M. Odén, M. J. H. Senna, J. E. Greene, and I. Petrov, *J. Appl. Phys.* 91 (2002) 3589.
- [8] J. R. Frederick and D. Gall, *J. Appl. Phys.* 98 (2005) 054906.
- [9] A. R. Smith, R. M. Freestra, D. W. Greve, A. Ptak, T. H. Myers, M. -S. Shin, M. Skowronski, *MRS Internet J. Nitride Semicond. Res.* 3 (1998) 12.
- [10] Z. Zhang and M. G. Lagally, *Science* 276 (1997) 377.
- [11] P. Politi, G. Grenet, A. Marty, A. Ponchet and J. Villain, *Phys. Rep.* 324 (2000) 271.
- [12] J. W. Evans, P. A. Thiel and M. C. Bartelt, *Surf. Sci. Rep.* 61 (2006) 1.

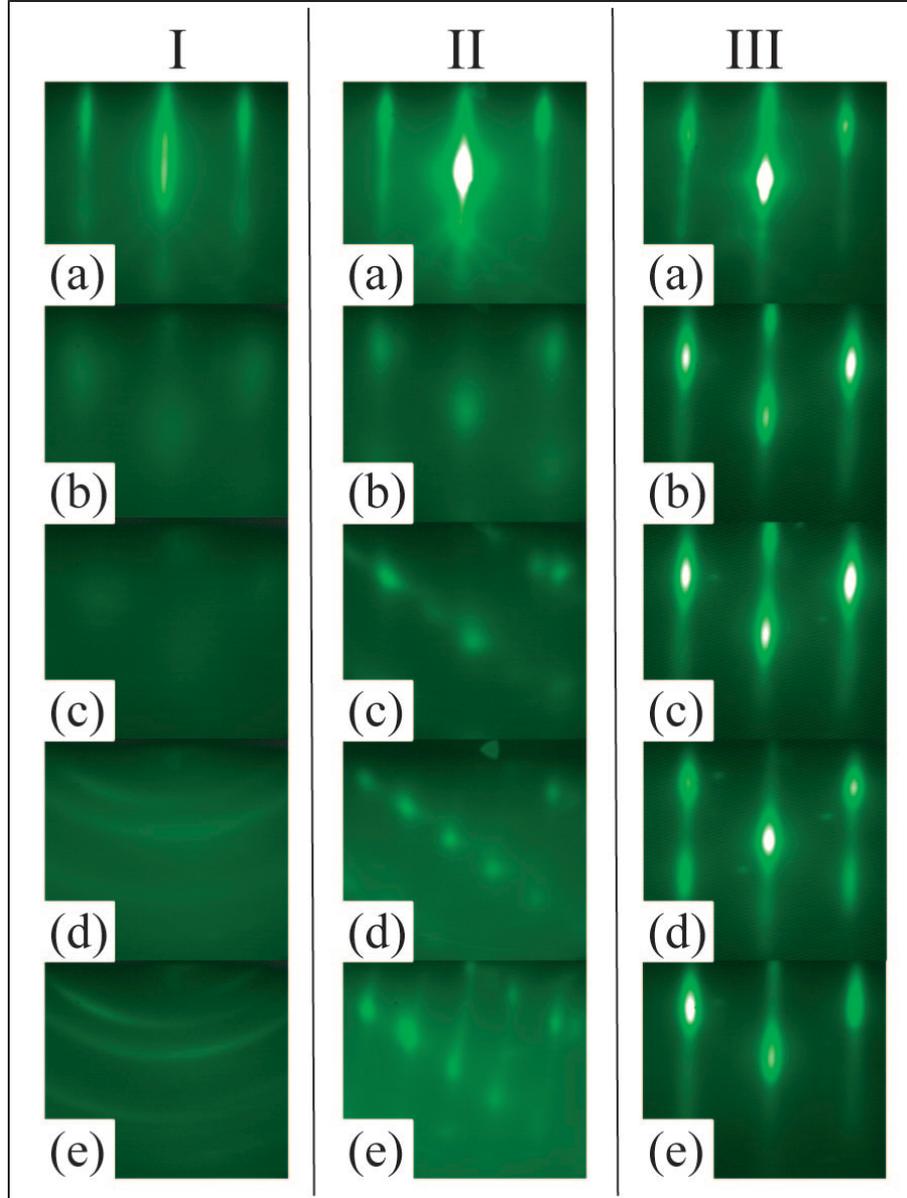


Figure 1: (Color online.) Evolution of RHEED patterns taken along direction [110] with the growth time for samples grown under different conditions. Panel I is for Sample A grown at a temperature ~ 220 °C with a flux ratio of $f_N/f_{Cr}=3/2$. Panel II is for sample B initially grown at 430 °C with a flux ratio $f_N/f_{Cr}=3/2$. Panel II(d) and (e) correspond to the additional growth of sample B at 650 °C for 30 seconds and 40 minutes, respectively. Panel III is for sample C grown at 430 °C with a flux ratio $f_N/f_{Cr}=10$. In all three panels, the row (a) corresponds to the RHEED patterns of MgO(001) substrate while rows (b)-(e) correspond to RHEED patterns of CrN(001) films. The details are shown in the text.

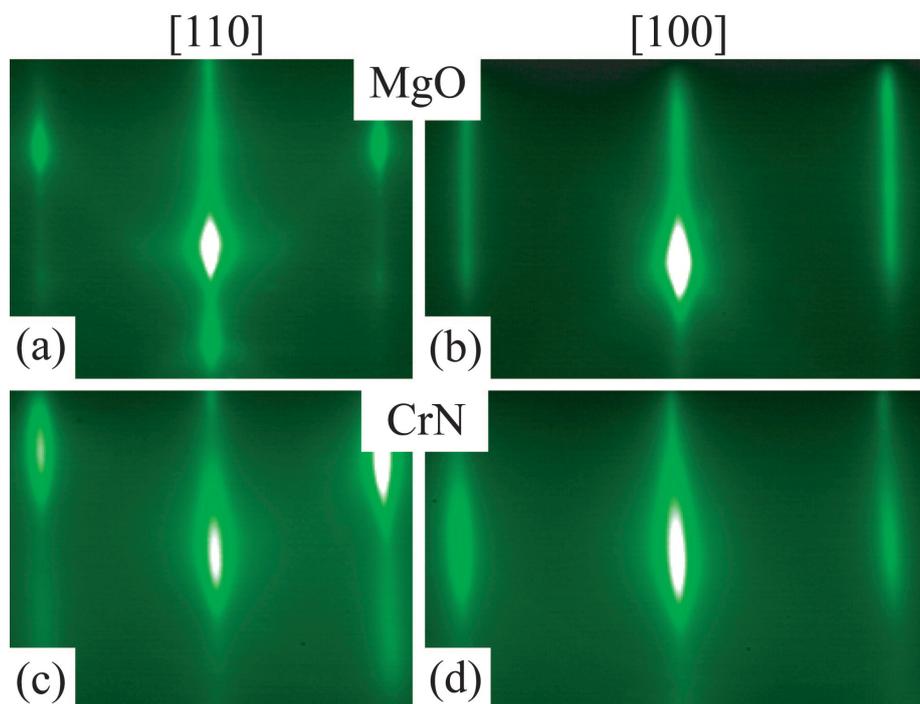


Figure 2: (Color online.) RHEED patterns taken along (a) [110] and (b) [100] directions of MgO(001) substrate that is annealed at 1000 °C for one hour. RHEED patterns for epitaxially grown sample D (37 nm) on MgO(001) substrate taken along (c) [110] and (d) [100] directions, respectively.

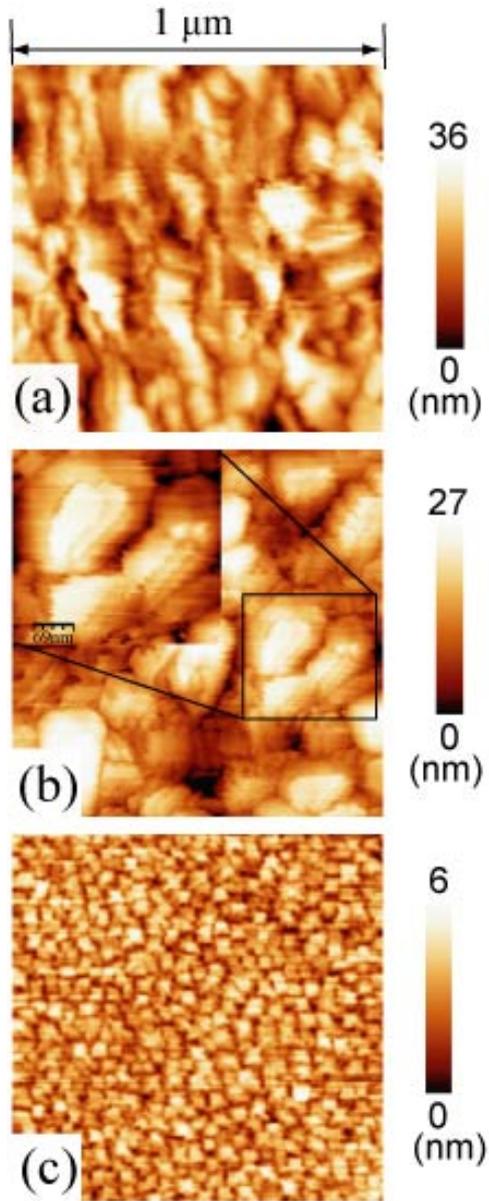


Figure 3: (Color online.) Atomic micrographs with dimension of $1\mu\text{m}\times 1\mu\text{m}$ measured on CrN(001) thin films grown under various conditions. (a) Sample A grown at $220\text{ }^\circ\text{C}$ with $J_N/J_{Cr}=3/2$. (b) Sample B grown at $430\text{ }^\circ\text{C}$ with $J_N/J_{Cr}=3/2$. (c) Sample C grown at $430\text{ }^\circ\text{C}$ with $J_N/J_{Cr}=10$.

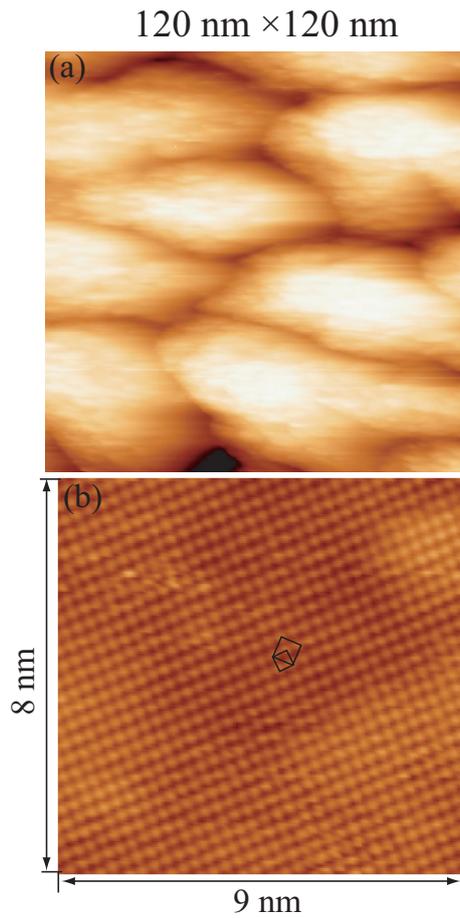


Figure 4: (Color online.) Topographic STM images measured *in situ* at room temperature with the constant-current mode. (a) One large-area STM image obtained on sample D at a tunneling current 0.29 nA and a bias voltage 0.8 V. (b) Part of an atomically resolved STM image measured at a tunneling current 0.64 nA and a bias voltage 0.93 V.

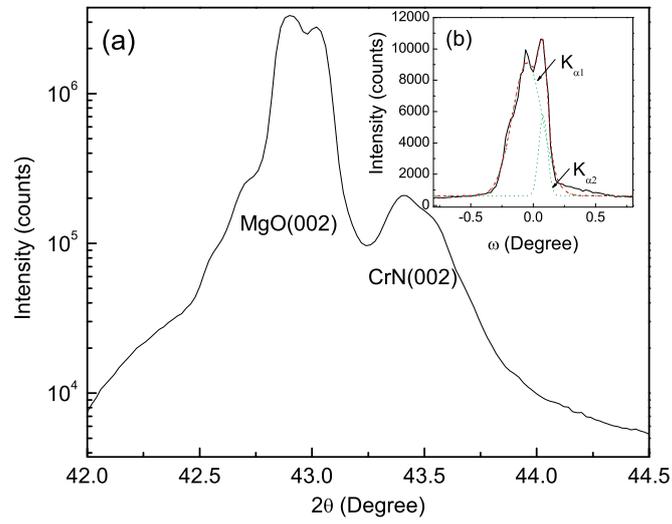


Figure 5: (Color online.) XRD patterns of sample C measured at room temperature. (a) Traditional θ - 2θ scan in a range from 42.0° to 44.5° . (b) The rocking curve scan. The solid line is the experimental data and the dashed line is the Lorentzian fit using two peaks: one for Cu $K_{\alpha 1}$ and the other for Cu $K_{\alpha 2}$. The FWHM for Cu $K_{\alpha 1}$ is about 0.24° .