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Annealing Process-Induced Microstructural Variation in NiV/B₄C Multilayers

Chenyuan Chang ^{1,†} , Zhenbo Wei ^{1,†}, Zhe Zhang ^{1,*} , Li Jiang ^{1,*} , Hui Jiang ² , Hongchen Ma ¹, Zhong Zhang ¹ and Zhanshan Wang ¹

¹ Key Laboratory of Advanced Micro-Structured Materials, MOE, Institute of Precision Optical Engineering, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China; 2010551@tongji.edu.cn (C.C.); weizb@tongji.edu.cn (Z.W.); 2110700@tongji.edu.cn (H.M.); zhangzhongcc@tongji.edu.cn (Z.Z.); wangzs@tongji.edu.cn (Z.W.)

² Shanghai Synchrotron Radiation Facility, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201204, China; jiangh@sari.ac.cn

* Correspondence: zzzfight1226@foxmail.com (Z.Z.); 1986jiangli@tongji.edu.cn (L.J.)

† These authors contributed equally to this work.

Abstract: The annealing process is one of the most common methods used to study the thermal stability of multilayers. To study the effect of the annealing process on the microstructural variation in NiV/B₄C multilayers, different annealing experiments were performed on NiV/B₄C multilayers with a d-spacing of 8 nm. This work provides a foundation for the fabrication of non-periodic NiV/B₄C multilayers. The NiV/B₄C multilayers were investigated by grazing-incidence X-ray reflectometry (GIXR), X-ray diffuse scattering (XRS), atomic force microscopy (AFM), X-ray diffraction (XRD), grazing-incidence small-angle X-ray scattering (GISAXS) and transmission electron microscopy (TEM). The temperature-dependent experiments showed that annealing at 70–290 °C slightly increased the period thickness and interface width. Annealing at higher temperatures resulted in significant structural changes and thickness ratio ($\Gamma = d_{\text{NiV}}/d$) changes from 0.4 to 1/3 at 340 °C. The time-dependent results showed that the microstructural variations primarily occurred after 60 min. The XRD, XRS, GISAXS and TEM were further used to study microstructural changes. It was found that the NiV/B₄C multilayers exhibited a microcrystal structure after annealing, and that enhanced crystallinity and an increase in interface roughness were the main reasons for the microstructural changes.

Keywords: microstructure; annealing; interface roughness; crystallinity; GISAXS



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1. Introduction

Multilayer optical elements have attracted widespread interest due to their special optical properties for application in fields such as plasma diagnostics and astronomical observation projects [1–5]. Nickel is considered one of the ideal materials for absorbing hard X-rays, as it lacks absorption lines in the 10 to 200 keV energy range. The Ni_{0.93}V_{0.07} alloy overcomes the issue of nickel's magnetism, which hinders its compatibility with magnetron sputtering. The NiV/B₄C combination, characterized by higher reflectivity and smaller interface roughness, was recommended by the Danish Space Institute [6] for high-energy optical systems and was first implemented at the European Synchrotron Radiation Facility (ESRF) in 2017 [7]. Although the NiV/B₄C combination has received extensive attention, the challenge of fabricating a high performance NiV/B₄C multilayer has limited its development due to interface defects during deposition, which can affect the optical properties and stability of multilayers. To ensure the robustness of NiV/B₄C multilayers, the multilayers were usually annealed to change their microstructures. Therefore, it is essential to comprehend the impact of annealing on the microstructure and properties of multilayers [8,9].

Annealing is a widely used method to improve the microstructural performance of deposited multilayers [10]. Many studies have been performed to analyze the microstructural changes in multilayers during annealing. For example, Saša Bajt et al. [9] prepared W/SiC and WC/SiC multilayers with period thicknesses ranging from 3.8 nm to 28 nm and annealed at 100 °C to 900 °C. They observed that the thickness of short-period multilayers expanded while the large-period multilayers were contracted. The interface roughness of the W/SiC multilayers increased after annealing. The microstructure of the W/SiC multilayers after annealing was further analyzed by X-ray diffraction (XRD). The results showed that the W/SiC multilayers crystallized when the period thickness reached 5.8 nm, and the crystallization was enhanced by further annealing. They attributed the variations in thickness and interface roughness to fluctuations in the density of the film layer. Tai D et al. [11] annealed Ru/C multilayers at 500 °C ($d = 2, 5$ and 10 nm). They found that the multilayers of different period thicknesses were expanded after annealing. Crystallization occurred in the multilayers with period thicknesses of 5 and 10 nm after annealing. To further study the effect of period thickness on thermal stability, Tai D et al. [12] annealed a Ru/C multilayer with a d -spacing of 3.5 nm at 600 °C. The results showed that the crystallization of the multilayers after annealing led to an increase in the period thickness, and this expansion increased the interface roughness. Huang et al. [13] prepared a W/Si multilayer with a d -spacing of 3.8 nm. The reflectivity and structure of the multilayer was studied after annealing. They found that the reflectivity of the multilayer was increased after annealing at 150 °C. In addition, higher temperature heat treatment led to a decrease in the reflectivity of the W/Si multilayer. Previous studies showed that microstructural changes would happen during the annealing process. The changes within the layers or at the interfaces of the multilayers resulted in microstructural changes. The detailed information about the interface of the multilayer was an effective way to monitor the microstructure of the multilayer, which requires advanced testing techniques. However, traditional methods of microstructure characterization are costly and can cause damage to samples.

For the analysis of interface roughness and diffusion, the grazing-incidence small-angle X-ray scattering (GISAXS) measurements were used. Saldit et al. showed that the GISAXS technology could achieve unambiguous interface characterization without destroying the sample [14,15] and was sensitive to determining the correlation length [16]. In our recent work [17], GISAXS was used to study the microstructural evolution of the NiV/B₄C multilayers ($d = 3$ nm) after annealing. We found that the amorphous NiV/B₄C multilayers (as-deposited) were crystallized after annealing. The interface roughness of NiV/B₄C multilayers increased with higher annealing temperatures or prolonged annealing times, while the lateral correlation length decreased. As the thickness of the multilayers increased, the metal layer transitioned from an amorphous to a crystalline state. The thickness of the multilayer at which the phase transition from amorphous to crystalline occurred was known as the critical crystallization thickness [11,17,18]. In our recent work [17], the microstructure evolution of NiV/B₄C multilayers ($d = 3$ nm) after annealing was analyzed by GISAXS and X-ray scattering. We found that the amorphous NiV/B₄C multilayers (as-deposited) were crystallized after annealing. The interface parameters such as interface roughness and lateral correlation length were obtained by fitting the PSD function. We found that the interface roughness of NiV/B₄C multilayers increased with higher annealing temperatures or prolonged annealing times, while the lateral correlation length decreased. As the thickness of the multilayers increased, the metal layer transitioned from an amorphous to a crystalline state. The thickness of the multilayer at which the phase transition from amorphous to crystalline occurred was known as the critical crystallization thickness [11,17,18]. Therefore, to further understand the effect of annealing on the properties of NiV/B₄C multilayers, the microstructure of NiV/B₄C multilayers with a period of 8 nm under different annealing conditions was systematically studied in this paper.

2. Materials and Methods

The NiV/B₄C multilayers were deposited on 20 mm × 20 mm super-polished silicon wafers by a direct current magnetron sputtering system. The base pressure was 8×10^{-5} Pa during the deposition. The multilayers consisted of 30 NiV/B₄C bilayers with the period thickness $d = 8$ nm and the NiV layer thickness to period thickness ratio of $\Gamma = d_{\text{NiV}}/d = 0.4$. The target materials used for sputtering included a B₄C target with 99.5% purity and a NiV target with 99.99% purity. The NiV target was composed of 93% nickel and 7% vanadium. The sputtering powers of the NiV and B₄C targets are on the order of tens of watts, with the distance between the sputtering targets and the substrate being approximately 80 cm. Argon was used as the working gas at a pressure of 0.16 Pa during the deposition, ensuring that the deposited atoms have high kinetic energy and form a smooth interface. The thickness of each layer in the multilayer was adjusted by controlling the sputtering time of each target. The deposited samples were annealed for 60 min in a high-vacuum (less than 5×10^{-4} Pa) at temperatures of 70, 140, 220, 290, and 340 °C, respectively. We also annealed some samples at 340 °C for different annealing times, specifically 10, 30, 60, and 120 min. The temperature control curve is consistent with previous studies of NiV/B₄C multilayers with a period of 3 nm.

The structures of NiV/B₄C multilayers were characterized by X-ray reflectometry (GIXR) and XRD measurements. For the GIXR and XRD experiments, we employed a Bruker D8 DISCOVER X-ray diffractometer with Cu-K α radiation. The rocking curve scans were performed around the first Bragg peak of the multilayers. The surface roughness of the sample was measured using a Bruker Dimension Icon Atomic Force Microscope (AFM). Each sample was scanned at two different locations, with each scan covering an area of $2 \mu\text{m} \times 2 \mu\text{m}$, with 512×512 data points scanned using fast axis X and slow axis Y. The GISAXS measurements were carried out at the BL16B1 beamline station of the Shanghai Synchrotron Radiation Facility (SSRF). The scattering intensity was measured using a two-dimensional Pilatus 3X 2M detector with an X-ray energy of 10 keV. The exposure time was set to 10 s to avoid detector saturation. The small angle of incidence θ_i was set to 0.35° , between total external reflection and the first Bragg peak. The NiV/B₄C multilayers were placed at the sample table [17]. The annealed multilayer was characterized using a JEM-ARM300F transmission electron microscope from JEOL, Tokyo, Japan, equipped with a double spherical aberration corrector. The electron acceleration voltage was 300 kV, and the point resolution was 0.08 nm. The microstructure and crystalline state of the annealed multilayer was analyzed through transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurements.

3. Results and Discussion

3.1. Grazing-Incidence X-Ray Reflectometry Analysis (Different Annealing Temperatures)

The GIXR curves and fitted curves of all NiV/B₄C multilayers before and after annealing are shown in Figures 1a and 1b, respectively. The grazing angles of the Bragg peaks progressively decreased as the annealing temperature increased from 70 °C to 340 °C, which suggesting an expansion in the multilayer d-spacing thickness. Notably, the third Bragg peak of the NiV/B₄C multilayer disappeared after annealing at 340 °C, indicating that the thickness ratio was 1/3.

As shown in Figure 1, based on the GIXR results, we inferred that the structural changes in the NiV/B₄C multilayers were attributed to variations in annealing temperature, as all other deposition and measurement parameters remained constant. The structural parameters of the NiV/B₄C multilayer films were quantitatively determined using the film simulation software IMD Version 5.0 [19]. The detailed results are shown in Tables 1 and 2. The changes in period and interface width before and after annealing of NiV/B₄C multilayers are shown in Figures 2a and 2b, respectively. The results indicate that the interface width increased with rising annealing temperatures, which was caused by the interface roughness and diffusion. Additionally, the increase in the periodic thickness of NiV/B₄C multilayers after annealing may be caused by the expansion of boron carbide [20,21].

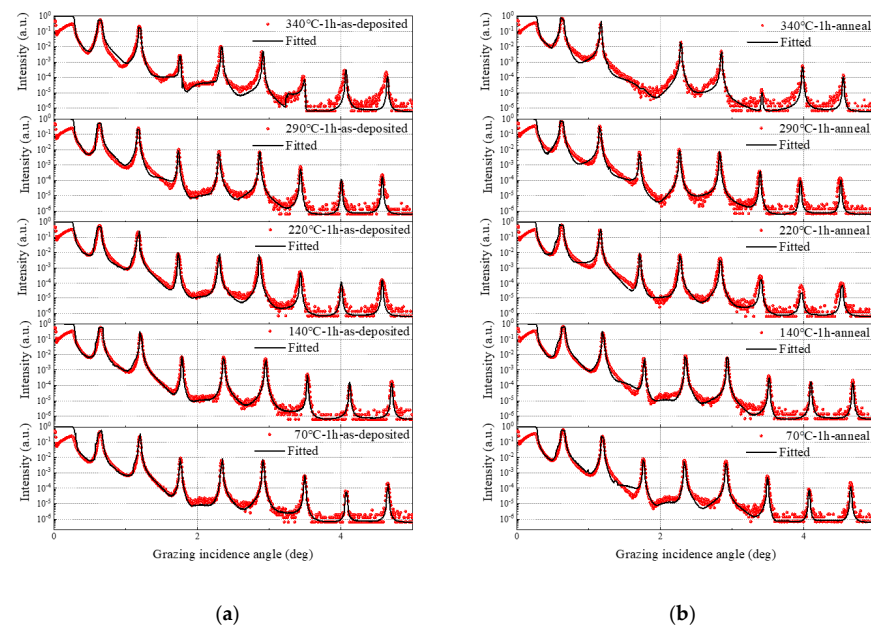


Figure 1. The GIXR curves and fitted curves: (a) before annealing, (b) after annealing.

Table 1. Quantitative fitting results of the thickness before and after annealing with equal time.

Temperature (°C)	Periodic Thickness d (nm)		Layer Thickness d (nm)				Δd_{NiV} (nm)	$\Delta d_{\text{B}_4\text{C}}$ (nm)
	As-Deposited	Annealed	As-Deposited		Annealed			
			d_{NiV} (nm)	$d_{\text{B}_4\text{C}}$ (nm)	d_{NiV} (nm)	$d_{\text{B}_4\text{C}}$ (nm)		
70	7.613	7.635	2.301	5.312	2.309	5.326	0.008	0.014
140	7.552	7.596	2.300	5.252	2.317	5.279	0.017	0.026
220	7.785	7.855	2.397	5.388	2.425	5.430	0.028	0.042
290	7.752	7.852	2.381	5.371	2.422	5.430	0.041	0.059
340	7.724	7.843	2.609	5.115	2.650	5.193	0.041	0.078

Table 2. Quantitative fitting results of the interface width before and after annealing with equal time.

Temperature (°C)	Interface Width σ (nm)				$\Delta\sigma_{\text{NiV-on-B}_4\text{C}}$ (nm)	$\Delta\sigma_{\text{B}_4\text{C-on-NiV}}$ (nm)
	As-Deposited		Annealed			
	$\sigma_{\text{NiV-on-B}_4\text{C}}$ (nm)	$\sigma_{\text{B}_4\text{C-on-NiV}}$ (nm)	$\sigma_{\text{NiV-on-B}_4\text{C}}$ (nm)	$\sigma_{\text{B}_4\text{C-on-NiV}}$ (nm)		
70	0.304	0.304	0.307	0.306	0.003	0.002
140	0.302	0.311	0.307	0.316	0.006	0.004
220	0.292	0.292	0.301	0.299	0.009	0.007
290	0.275	0.310	0.287	0.320	0.012	0.009
340	0.270	0.275	0.291	0.293	0.021	0.017

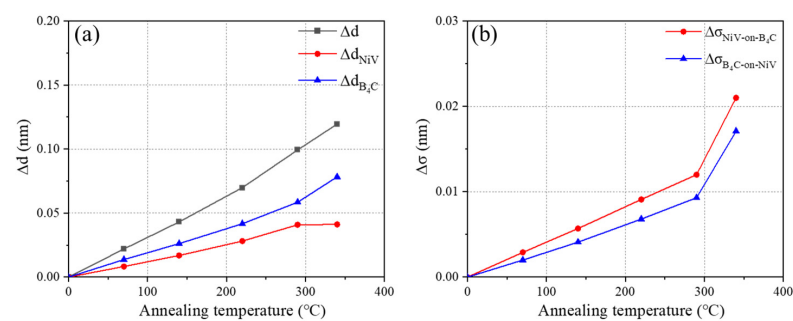


Figure 2. The changes in (a) periodic thickness and (b) interface width before and after annealing.

3.2. Grazing-Incidence X-Ray Reflectometry Analysis (Different Annealing Times)

The GIXR curves and fitted curves of all samples are shown in Figures 3a and 3b, respectively. With the extension of annealing time, the angle of the Bragg peak decreased, indicating an increase in period, as shown in Figure 4a. The interface width also increased with longer annealing times, as shown in Figure 4b. Compared to the first experiment (different annealing temperatures), the second experiment (different annealing times) more clearly demonstrated changes in the thickness ratio of the multilayers. Notably, when the annealing time was extended to 120 min, the third-order Bragg peak reappeared. The fitted structural parameters are shown in Tables 3 and 4.

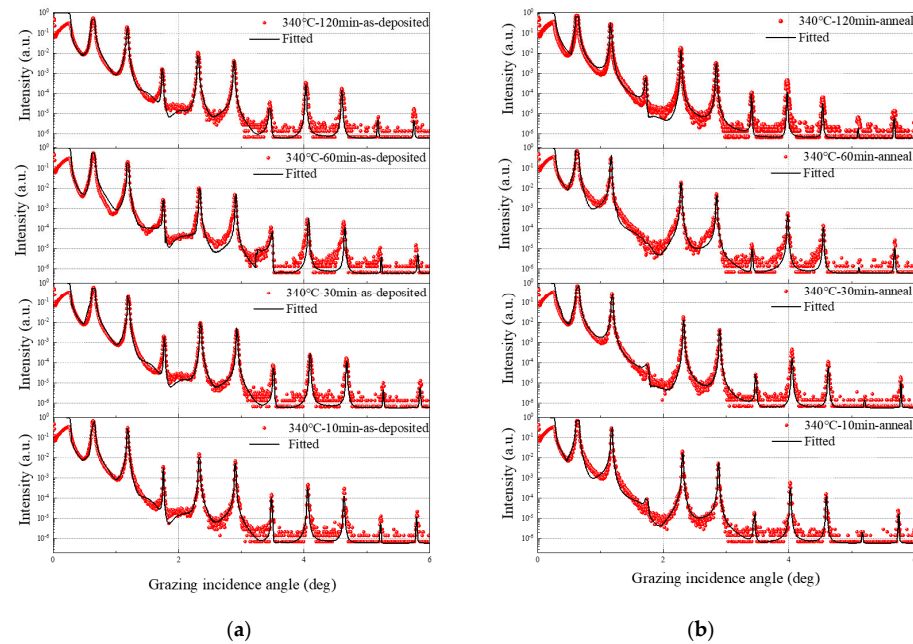


Figure 3. The GIXR curves and fitted curves: (a) before annealing, (b) after annealing.

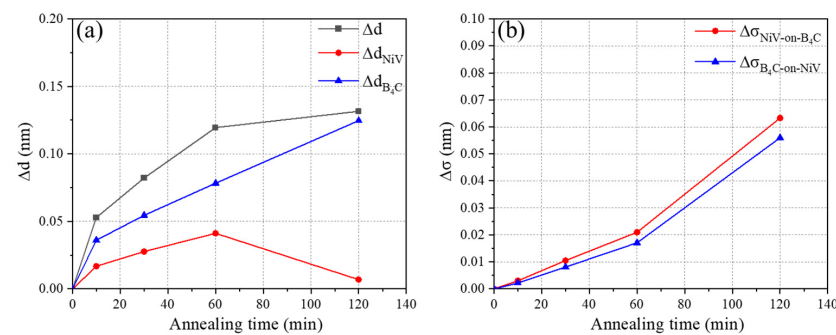


Figure 4. The relative changes in (a) periodic thickness and (b) interface width.

Table 3. Quantitative fitting results of the thickness before and after annealing at 340 °C.

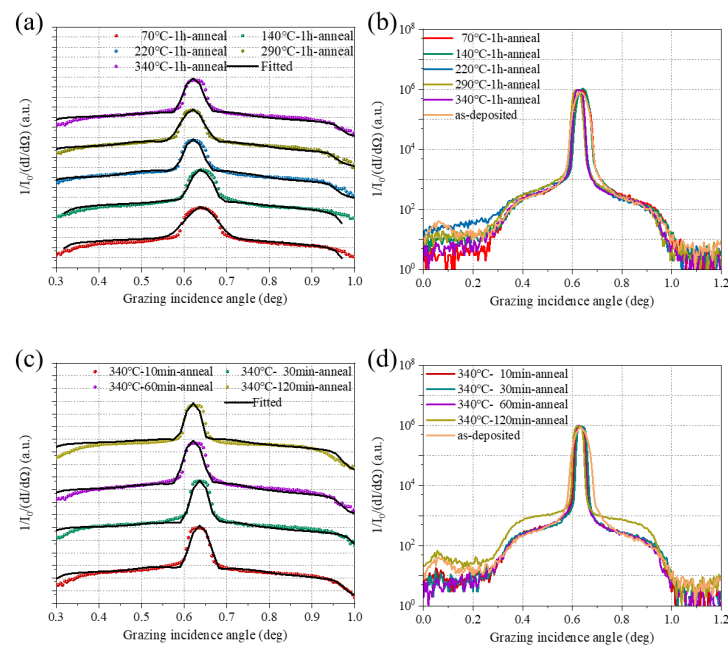
Time (min)	Periodic Thickness d (nm)		Layer Thickness d (nm)				Δd_{NiV} (nm)	$\Delta d_{\text{B}_4\text{C}}$ (nm)
	As-Deposited	Annealed	As-Deposited		Annealed			
			d_{NiV} (nm)	$d_{\text{B}_4\text{C}}$ (nm)	d_{NiV} (nm)	$d_{\text{B}_4\text{C}}$ (nm)		
10	7.667	7.720	2.586	5.081	2.603	5.117	0.017	0.036
30	7.596	7.679	2.561	5.035	2.589	5.090	0.028	0.055
60	7.724	7.843	2.609	5.115	2.650	5.193	0.041	0.078
120	7.704	7.836	2.481	5.223	2.488	5.348	0.007	0.125

Table 4. Quantitative fitting results of the interface width before and after annealing at 340 °C.

Time (min)	Interface Width σ (nm)				$\Delta\sigma_{\text{NiV-on-B}_4\text{C}}$ (nm)	$\Delta\sigma_{\text{B}_4\text{C-on-NiV}}$ (nm)
	As-Deposited		Annealed			
	$\sigma_{\text{NiV-on-B}_4\text{C}}$ (nm)	$\sigma_{\text{B}_4\text{C-on-NiV}}$ (nm)	$\sigma_{\text{NiV-on-B}_4\text{C}}$ (nm)	$\sigma_{\text{B}_4\text{C-on-NiV}}$ (nm)		
10	0.270	0.291	0.273	0.293	0.003	0.002
30	0.260	0.284	0.270	0.292	0.011	0.008
60	0.270	0.275	0.291	0.293	0.021	0.017
120	0.290	0.295	0.353	0.351	0.063	0.056

3.3. X-Ray Scattering Analysis

The X-ray scattering of NiV/B₄C multilayers was measured by a means of rocking curve scan to study changes in interface roughness. The scattering curves and fitted curves of all the NiV/B₄C multilayers before and after annealing are shown in Figure 5. The peak height represented the level of interface roughness. In Figure 5b, there was no obvious change in the scattering intensity of the NiV/B₄C multilayers, which indicated that the interface roughness changed slightly. The scattering peaks were significantly enhanced at 340 °C for 120 min, indicating an increase in interface roughness, as shown in Figure 5d. The X-ray scattering measurements were fitted by IMD software Version 5.0. As shown in Figure 5a,c, the fitting curves closely matched the rocking curve scans, implying that the fitting model accurately reflected the multilayer structure. The lateral correlation length and interface roughness information of X-ray scattering data were quantitatively fitted by IMD, and the results are shown in Table 3.

**Figure 5.** Rocking curve scans of NiV/B₄C multilayers: (a) measurements and fitted curves, (b) set of measurements at different temperatures, (c) measurements and fitted curves, (d) set of measurements for different times.

3.4. X-Ray Diffraction Analysis

The results of GIXR and X-ray scattering measurements showed that an increase in interface width was observed when the multilayers were annealed at different temperatures. We conjectured that the annealing process changed the microstructure of the multilayers, leading to increased interface roughness and period thickness.

The crystallization was confirmed by XRD measurements, and the results are shown in Figure 6. In Figure 6, a (0 0 1) crystal plane diffraction peak of V_5O_9 appeared at $2\theta = 11.453^\circ$, and no other sharp peaks were present when the annealing time was less than 120 min. This is consistent with previous research [22]. The crystal plane diffraction peaks of B_2O (0 0 1) (PDF#41-0624) appeared at $2\theta = 12.530^\circ$ and a crystalline phase of Ni_5V appeared at a smaller angle after annealing for 120 min [23]. With the increase in annealing temperatures, the (0 0 1) peak position of V_5O_9 moved to a lower 2θ , indicating that the crystallinity increased.

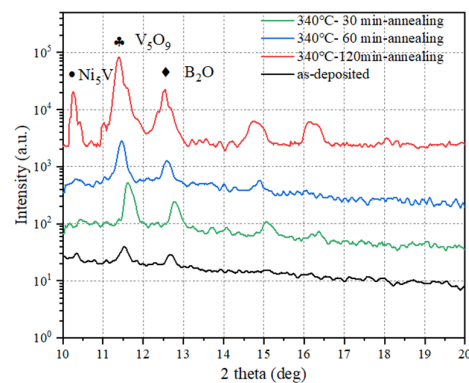


Figure 6. XRD patterns of the NiV/ B_4C multilayers annealed under different conditions.

3.5. Atomic Force Microscope Analysis

In Figure 7, comparisons of atomic force microscopy (AFM) measurements of the NiV/ B_4C multilayers are shown at $340^\circ C$ for different annealing times. To improve the accuracy of statistical information, the surfaces of all samples were measured several times at different spots. The average rms values of the NiV/ B_4C multilayers were $r_q \approx 0.124$ nm with annealing time less than 120 min. The rms value for the 120 min annealing sample was $r_q = 0.359$ nm. Significantly, after 120 min of annealing, uniform bright spots appeared on the surface of the multilayer film, which were caused by the crystallization of the multilayer. This was consistent with the XRD results above.

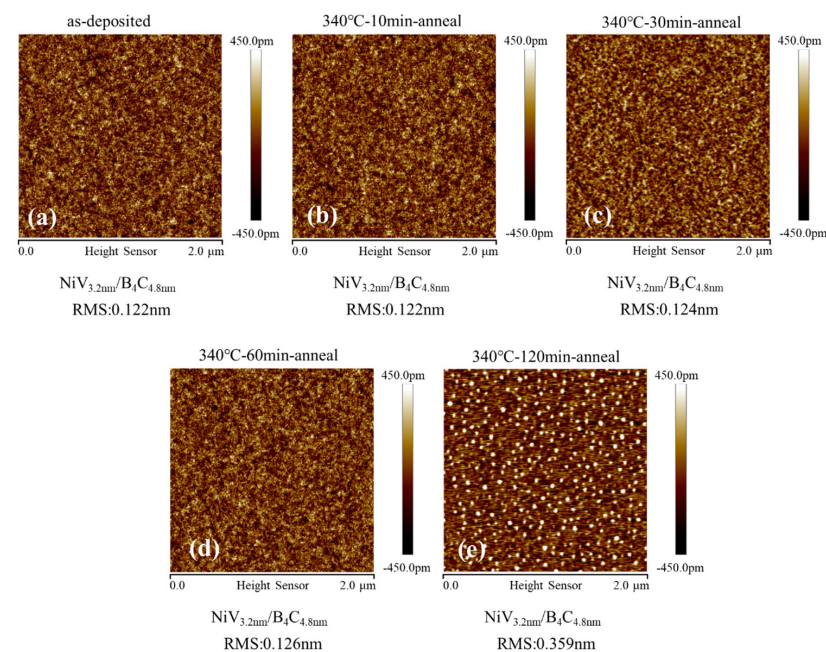


Figure 7. AFM data of the multilayers annealed at different times: (a) as-deposited, (b) annealing at $340^\circ C$ for 10 min, (c) annealing at $340^\circ C$ for 30 min, (d) annealing at $340^\circ C$ for 60 min, (e) annealing at $340^\circ C$ for 120 min.

3.6. Grazing-Incidence Small-Angle X-Ray Scattering Analysis

The core principle of GISAXS measurement is to collect spatial distribution information on scattered light intensity that deviates from the reflection direction. In actual multilayer structures, the complex surface and interfaces contribute to the observed scattered light distribution, which is the result of the combined effect of these interfaces. To accurately analyze the X-ray scattering information, researchers typically use the distorted wave Born approximation (DWBA) theory [22]. According to the DWBA model, the transformation of the X-ray from an incident wave (initial state) to a scattered wave (final state) at any interface is primarily driven by surface roughness or perturbation potential due to diffusion within the material. The perturbation theory treats the scattering amplitude as a power series of roughness height, making it possible to associate the scattering amplitude with the power spectral density (PSD) function without making any assumptions about the roughness height distribution. The average interface statistics can be determined using the integral method of perturbation theory, and the specific formula derivation can be seen in our previous work [17].

The GISAXS measurements of the NiV/B₄C multilayers are shown in Figure 8a. The most obvious feature of GISAXS is the Bragg sheet [14] caused by the correlated interface roughness [24]. As the annealing temperature increases, the shapes of the Bragg sheets for the NiV/B₄C multilayers slightly broaden with no changes in the number of Bragg sheets. However, annealing at 340 °C, the third Bragg sheet disappeared, indicating that the structure of the multilayer had changed. To investigate the process involved in this change, multilayer samples annealed at 340 °C for different times were tested. We found that after annealing at 340 °C for 10 min, the third Bragg sheet almost disappeared, and it disappeared completely at 60 min. When the annealing time reached 120 min, the third Bragg sheet reappeared and showed stronger scattering intensity. In Figure 8b,c, as the annealing temperature increases and the annealing time extends, the number of Bragg-like peaks of the NiV/B₄C multilayers remains at five. However, the peak shapes and positions of the multilayers have changed, indicating that the thickness of the multilayers had changed. Combining the GIXR results, we found that the thickness of the NiV/B₄C multilayers gradually increased throughout the annealing process. This result showed that it was not purely physical expansion; a chemical reaction took place at its interface [23].

In Figure 8d, an enhancement of the scattering outside the Bragg sheets can be seen [25,26], which is more apparent in Figure 8a. In Figure 8d, the small peaks on both sides of the annealed sample correspond to the density fluctuation distribution. The line extraction of the sample before annealing has no visible peak outside the $q_x = 0$ center, indicating that the sample does not have density fluctuations. Note that in the W/Si multilayer structure, similar density fluctuations are observed within the Si layer, which is attributed to the formation of crystals in the Si layer [26].

Figure 9 showed the PSD functions of the NiV/B₄C multilayers. The interface structure of the NiV/B₄C multilayers remained relatively stable as the annealing temperature increased, but the interfaces changed progressively with extension of the annealing time at 340 °C.

The parameters for interface roughness and lateral correlation length were obtained by quantitatively fitting the interface PSD function. The PSD functions and fitting curves of the NiV/B₄C multilayers before and after annealing are shown in Figure 9. As seen in Figure 9a,b, the PSD of the multilayers increased gradually with the rise in annealing temperature. As seen in Figure 9c,d, the PSD of the multilayers remained stable when the annealing time was less than 120 min, with an inflection point occurring at 120 min. At 120 min, the PSD curve increased with annealing time, indicating an increase in interface roughness. Table 5 and Figure 10 compared the lateral correlation length results obtained by the two test methods.

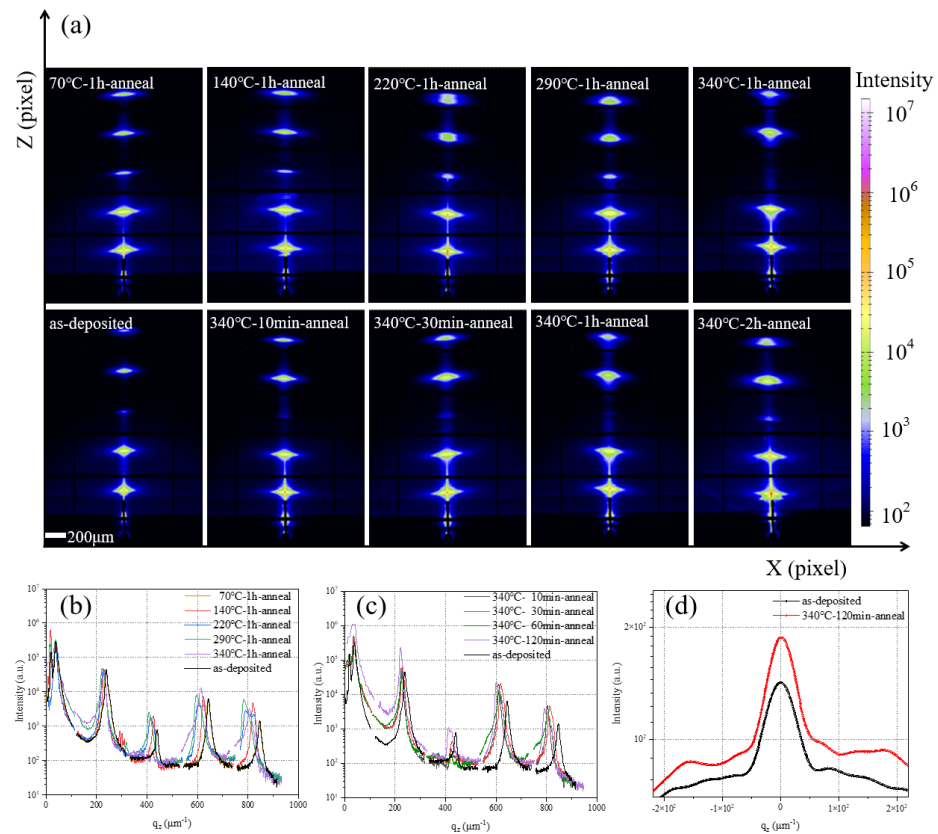


Figure 8. (a) GISAXS maps, the scattering curves against the wave vector q_z at (b) different temperatures and (c) different times, and (d) the line extractions in between the 2nd and the 3rd Bragg sheets along the q_x direction averaged in between Bragg sheets.

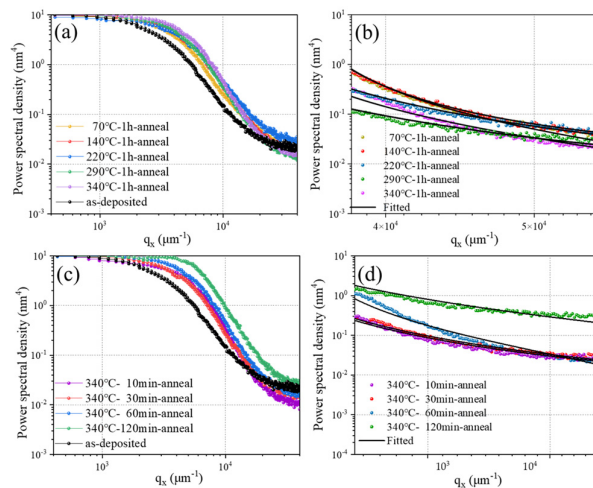
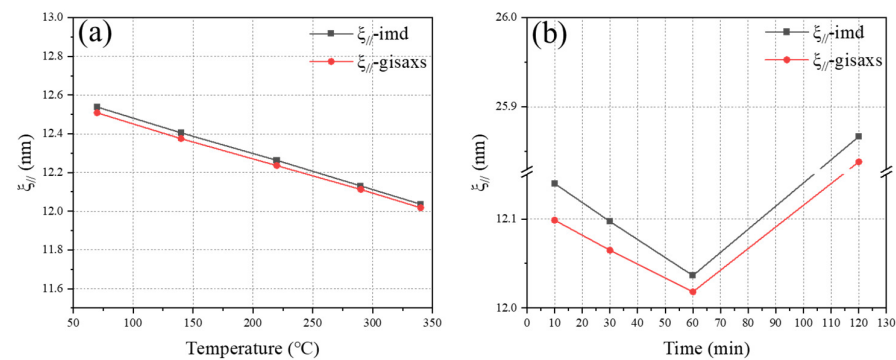


Figure 9. PSD functions of NiV/B₄C multilayers: (a) annealing at different temperatures, (b) fitted curves, (c) annealing for different times, and (d) fitted curves.

The results of GISAXS show that the interface roughness of NiV/B₄C multilayers exhibits an increased trend after annealing, and keeps a monotonic relationship with the variation in the lateral correlation length except with annealing at 340 °C for 120 min [17,25,26]. This is slightly different from our previous study on NiV/B₄C multilayers with the periodic thickness of 3 nm [17]. In combination with other tests above, we propose that the annealing process facilitates the crystallization of the multilayers, which increases the interface roughness and decreases the lateral correlation length. However, prolonged annealing time at high temperatures will cause recrystallization and increase the lateral correlation length.

Table 5. The lateral correlation length of NiV/B₄C multilayers after annealing.

Annealing Parameters	$\xi_{//\text{-IMD}}$ (nm)	$\xi_{//\text{-GISAXS}}$ (nm)	$\Delta\xi_{//}$ (nm)
70 °C for 60 min	12.539	12.509	0.030
140 °C for 60 min	12.405	12.375	0.030
220 °C for 60 min	12.263	12.236	0.027
290 °C for 60 min	12.131	12.113	0.018
340 °C for 60 min	12.037	12.018	0.018
340 °C for 10 min	12.140	12.099	0.041
340 °C for 30 min	12.097	12.065	0.032
340 °C for 60 min	12.037	12.018	0.018
340 °C for 120 min	25.867	25.838	0.028

**Figure 10.** The lateral correlation length (the black line is the result of IMD software, and the red line is the result of GISAXS): (a) annealing at different temperatures, (b) annealing for different times.

3.7. Transmission Electron Microscope Analysis

To study the underlying physics of the changes in lateral correlation length and interface roughness, the microstructure of the NiV/B₄C multilayer after annealing at 340 °C for 120 min was characterized by transmission electron microscopy (TEM). As shown in Figure 11, the bright layers were B₄C, and the dark layers were NiV. The periodic layered structure of the NiV/B₄C multilayers were well-defined through the low magnification images, which confirmed the results found by GIXR and GISAXS. The high-resolution image (Figure 11c–e) showed that the NiV/B₄C multilayer had relatively clear interfaces. In Figure 11, the top, middle, and bottom layers of the NiV/B₄C multilayer were aligned, and it was found that the thickness of the multilayer layers changed little from the bottom layer to the top layer, indicating that the multilayer was uniform overall after annealing, which was consistent with the GIXR results. After annealing, the interfacial diffusion of the multilayer films was not obvious, which indicated that the interfacial defects were dominated by the interface roughness. The weak crystallization of the NiV/B₄C multilayer was not easy to observe with TEM. The NiV/B₄C multilayer after annealing was micro-crystalline, and a slight diffraction ring could be seen in the selected electron diffraction in Figure 11b. This was consistent with the XRD results (Figure 6). To study the interface conditions after the annealing of the NiV/B₄C multilayer, the one-dimensional projection gray value results of the 2D TEM image were analyzed, and the results are shown in Figure 12. In previous studies [27], the interface width in grayscale maps has typically been defined as the middle portion of the transition region (30–70%). However, we believe this definition lacks sufficient precision. Therefore, we applied an error function to fit the grayscale information [19,28], which provides for more accurate determination of the interface width, and the interface widths were $\sigma_{\text{B}_4\text{C-on-NiV}} = 0.35$ nm and $\sigma_{\text{NiV-on-B}_4\text{C}} = 0.36$ nm, respectively, which were consistent with the GIXR results for $\sigma_{\text{B}_4\text{C-on-NiV}} = 0.35$ nm and $\sigma_{\text{NiV-on-B}_4\text{C}} = 0.35$ nm.

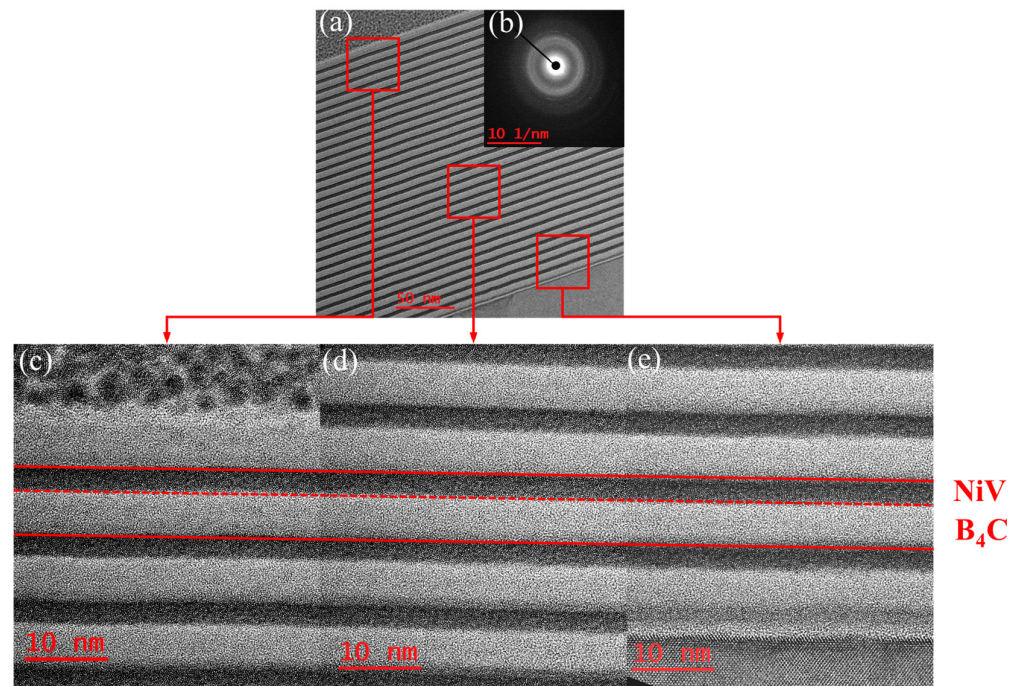


Figure 11. TEM data of the multilayers annealed at different parts: (a) TEM cross-section images, (b) SAED of (a), (c) TEM image of the upper part of the sample, (d) TEM image of the middle part of the sample, (e) TEM image of the bottom part of the sample.

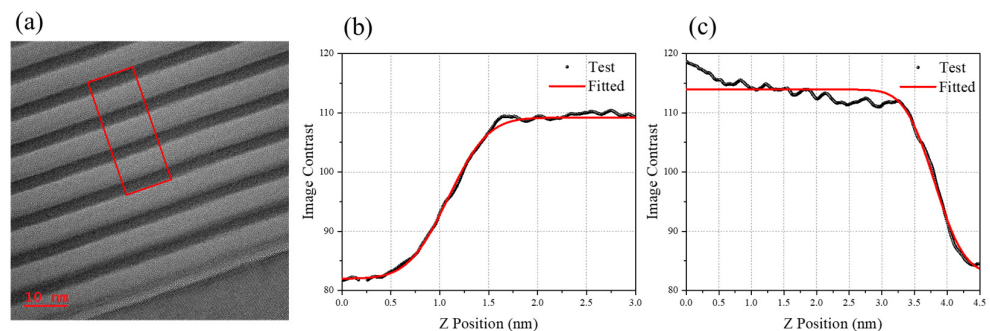


Figure 12. TEM gray scale image and fitting results: (a) grayscale information selection, (b) layer profiles and (c) fitting curve obtained from the images in the plane of the layer.

4. Conclusions

Previously, annealing of NiV/B₄C multilayers with a periodic thickness of 3 nm has shown that crystallization is the main cause of thickness expansion and greater interface roughness. To further study the microstructure changes in thicker annealed multilayers, NiV/B₄C multilayers with a period of 8 nm were prepared by the magnetron sputtering method, and two annealing experiments were carried out. The first group of annealing experiments were conducted with varying annealing temperatures at a constant annealing time, while the second involved different annealing times at a fixed annealing temperature. The main objective of this paper is to examine the impact of annealing on the microstructure of thicker NiV/B₄C multilayers, with the goal of offering insights to enhance the performance of these multilayers.

Temperature-dependent experiments show that annealing from 70 °C to 290 °C can slightly increase thickness and interface width. High temperature annealing results in significant structural changes. At 340 °C, the thickness of the film changes significantly, and the average interface width increases by 7%. The time-dependent results showed that most of the microstructure changes occurred mainly after 60 min. GISAXS and X-ray

scattering analysis show that the increase in interface width is mainly due to the increase in interface roughness, and the lateral correlation length is inversely proportional to the interface roughness. However, after annealing at 340 °C for 120 min, recrystallization and enhanced crystallization led to a significant increase in the transverse correlation length and interface roughness. These results differ slightly from those observed in previous studies on 3 nm multilayers. The XRD results show that the annealed NiV/B₄C multilayer films showed a microcrystalline structure, and the crystallization caused the change in film thickness and interface roughness, which was the main reason for the change in the microstructure of the multilayer films. AFM results show that after annealing at 340 °C for 120 min, the surface roughness of the multilayer films increases significantly and the crystalline morphology appeared on the surface, which is consistent with the results of XRD. By TEM test, it was found that the diffusion of the multilayer membrane was not obvious, and the overall state was microcrystalline. The gray value was analyzed by error function, and the interface width was close to the GIXR result. Therefore, we hypothesize that high-temperature annealing causes a substantial increase in the thickness of the multilayer, thereby facilitating the crystallization of the multilayer film. In addition, extending the high-temperature annealing time promotes the crystallization of multilayers. As a result, prolonged high-temperature annealing leads to the recrystallization of the multilayers, which enhances the crystal structure and subsequently increases the interface roughness and lateral correlation length. In view of this phenomenon, we plan to conduct thermal stability studies on multilayers with thicker film layers, aiming to establish a foundation for the development of non-periodic NiV/B₄C multilayers.

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