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The first successful growth of epitaxial twin-free nickel films on barium fluoride substrates

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For the first time, the growth of epitaxial twin-free nickel films on barium fluoride (BaF_2) substrates using magnetron sputtering has been demonstrated. It has been established that optimizing deposition conditions, including substrate temperature, working gas pressure, and sputtering power, enables the achievement of high structural perfection in the films. The obtained results open prospects for the application of such structures in magnetic and electronic devices.

Keywords: epitaxial films, twinning energy, X-ray diffraction analysis.

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Epitaxial nickel films attract research attention due to their unique magnetic and electrical properties and the potential for integration into heterostructures. Substrates with a cubic structure, such as Si [1], GaAs [2], Fe [3], Cu [4], or MgO [5–7], are traditionally used to grow such films. However, their lattice parameters do not always match perfectly with Ni, which leads to the formation of defects (including twins). Barium fluoride (BaF_2), which has a cubic structure with lattice parameter $a = 6.20$ Å, is a promising alternative, since it offers a less significant mismatch with Ni ($a = 3.52$ Å on conversion to a doubled cell). The present study is the first to detail the process of synthesis of epitaxial twin-free Ni films on BaF_2 by magnetron sputtering and their structural characteristics.

Films were deposited in a vacuum system with a base pressure of 10^{-6} Torr. A polycrystalline Ni plate with a purity of 99.99 % was used as a target. BaF_2 (111) substrates were cleaned in advance in an ultrasonic bath with isopropanol and annealed at 500 °C in vacuum to remove surface contaminants. Magnetron sputtering was carried out in an argon atmosphere (at a pressure of $5 \cdot 10^{-3}$ Torr) with a source power of 100 W. The substrate temperature was varied within the range of 300–600 °C, and the film thickness was 50–200 nm.

Structural analysis was performed using X-ray diffraction (XRD) methods. The X-ray diffraction pattern (Fig. 1, *a*) revealed the reflections of Ni (111), BaF_2 (111), and BaF_2 (222) only, which is indicative of epitaxial growth of films with the (111) orientation. The lack of additional peaks associated with twins or polycrystalline phases was confirmed at a substrate temperature of 450 °C. The half-width of the rocking curve (Fig. 1, *b*) was 0.23°, which is indicative of a high degree of structural perfection of the obtained films.

In addition, φ-scanning (i. e., measurement of reflection from the Ni (113) plane with the sample rotated about the normal to the substrate plane; see Fig. 2) was performed in order to determine the misorientation of the film in the substrate plane. The obtained pattern is indicative of third-order symmetry in the film, suggesting the lack of twins.

It turned out that it is critical to maintain the substrate temperature within a narrow range (430–470 °C): a polycrystalline structure formed at lower temperature levels, and diffusion of fluorine from BaF_2, which exerts a negative influence on the film quality, was observed at higher temperatures. The optimization of argon pressure ($5 \cdot 10^{-3}$ Torr) allowed us to minimize internal stresses, which also contributed to the suppression of twinning.

A comparison with traditional substrates, such as MgO ($a = 4.21$ Å), revealed that BaF_2 provides a less significant lattice mismatch (approximately 12 % versus 20 % for MgO), reducing the probability of defect formation.

Let us compare the dependences of twinning energy on the lattice mismatch value in the (111) plane for BaF_2 and MgO substrates.

Nickel: face-centered cubic (FCC) structure, lattice parameter $a_{Ni} = 3.52$ Å.

The interatomic distance in plane (111) is $d_{Ni(111)} = a_{Ni(111)}/\sqrt{2} = 3.52/\sqrt{2} \approx 2.49$ Å.

The stacking fault energy for bulk nickel is $\gamma_0 = 120–130$ mJ/m^2.

Barium fluoride (BaF_2): fluorite-type cubic structure, lattice parameter $a_{BaF_2} = 6.20$ Å.

The effective interatomic distance in plane (111) depends on the positioning of Ba and F atoms. For simplicity, we set the distance between barium atoms along (111) to

$$d_{BaF_2(111)} = a_{BaF_2(111)}/\sqrt{2} = 6.20/\sqrt{2} \approx 4.38 \text{ Å}.$$

The lattice mismatch in the (111) plane is calculated as $\varepsilon = |d_{subs(111)} - d_{Ni}(111)|/d_{Ni}(111)$. Inserting numerical values, we find $\varepsilon \approx 0.759$ (75.9 %). It would seem that

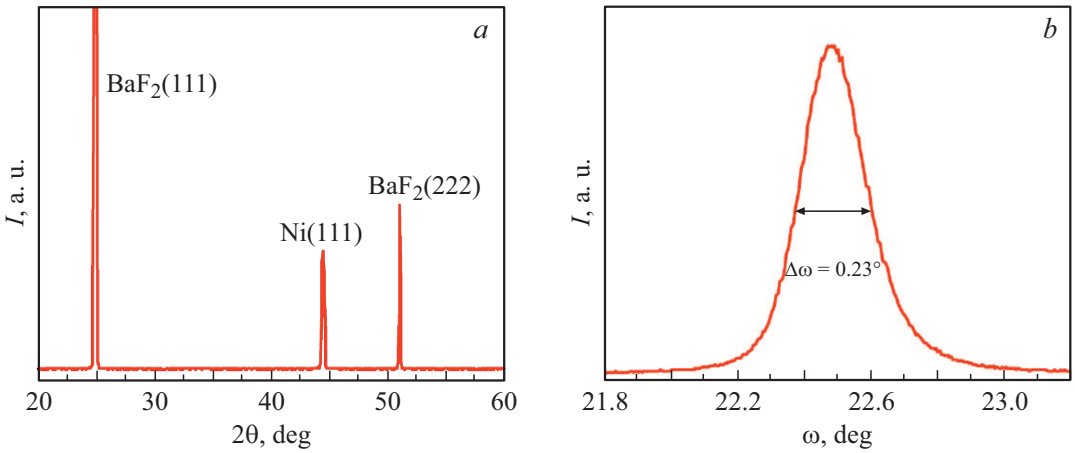

Figure 1. X-ray diffraction pattern (a) and rocking curve (b) of an 80-nm-thick Ni film deposited onto a barium fluoride substrate at a temperature of 450 °C.

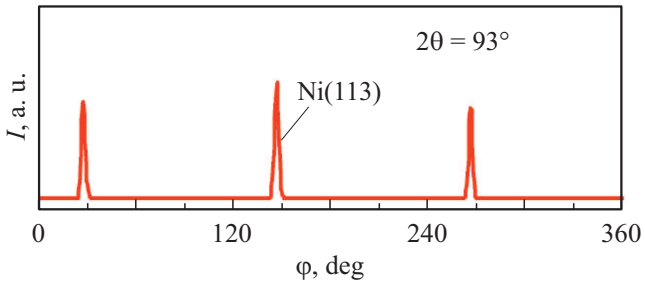

Figure 2. X-ray diffraction pattern for φ-scanning of the Ni/BaF_2 sample with a pitch of 1°.

the mismatch is very significant. However, in real-world systems, epitaxial growth is made possible by matching through multiples of parameters (i. e., when several nickel cells are aligned with one BaF_2 cell).

For example, the value for two Ni (111) cells ($2 \cdot 2.49$ Å) is closer to 4.38 Åand reduces the effective mismatch to $\varepsilon \approx 0.12$ (12 %).

Similar calculations for the MgO substrate yield a value of 0.20 (20 %).

Coherent (111) twins are the most common type of twins in fcc metals. The twinning energy (γ_t) is related to the stacking fault energy, since a twin may be regarded as a sequence of stacking faults. According to literature data (e. g., [8,9]), the stacking fault energy in Ni is $\sim 125-130\,\text{mJ/m}^2$. The twinning energy in an fcc structure is often set to $\gamma_t \approx 2\gamma_{sf}$ for a coherent twin, since it is equivalent to two stacking faults in adjacent layers. Let us take $\gamma_{sf} = 130\,\text{mJ/m}^2$ as the average value for Ni. The twinning energy is $\gamma_t = 260\,\text{mJ/m}^2$. The lattice mismatch induces elastic stresses that may reduce γ_t. We use the following simplified model for evaluation:

$$\Delta\gamma_t \approx -2k\varepsilon^2 E,$$

where ε is the strain due to mismatch (0.12 for a Ni film on BaF_2 or 0.20 for a film on MgO), E is the Young's modulus of nickel, and k is a geometry-dependent coefficient.

In real practice, $\Delta\gamma_t$ is corrected empirically and assumes a value on the order of $20\,\text{mJ/m}^2$ for systems with a mismatch on the order of 12 %.

The presented expression makes it evident that the twinning energy is proportional to the strain squared. Therefore, the change in twinning energy is approximately 2.8 times larger for films on magnesium oxide. Thus, for Ni/BaF_2 $\gamma_t = 240\,\text{mJ/m}^2$. The energy for Ni/MgO is $204\,\text{mJ/m}^2$.

Thus, the twinning probability is approximately 20 % lower when BaF_2 is used as a substrate.

For comparison purposes, nickel films were deposited onto MgO (111) substrates under similar conditions. Figure 3 presents the φ-scanning pattern for the obtained film.

The emergence of a small number of twins is evident, which confirms the results of comparative evaluation of the twinning probability.

Twin-free epitaxial nickel films on BaF_2 substrates have been obtained by magnetron sputtering for the first time. Optimized deposition conditions (temperature, 450 °C; pressure, $5 \cdot 10^{-3}$ Torr; power, 100 W) ensure high quality of heterostructures, which makes them promising for use in microelectronics and spintronics and for fabrication of twin-

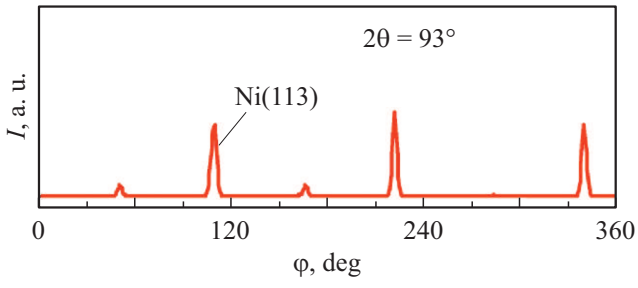

Figure 3. X-ray diffraction pattern for φ-scanning of the Ni/MgO sample with a pitch of 1°.

free graphene films by the well-known method of carbon diffusion through a nickel film. Further studies will be focused on the electrical properties of films and scaling up the process.

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Conflict of interest

The authors declare that they have no conflict of interest.

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