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STRESS RELAXATION THROUGH LOCAL MIGRATION OF INTERFACES IN NANOCRYSTALLINE COATINGS

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Abstract. A special mechanism of stress relaxation in nanocrystalline coatings is suggested and theoretically described. The mechanism represents the local migration of interfaces, first of all, grain boundaries (GBs), that occurs in athermal way and is accompanied by formation of wedge disclination quadrupoles in nanocrystalline coatings. The wedge disclination quadrupoles release, in part, mismatch stresses created at coating/substrate boundaries. It is theoretically shown that the special relaxation mechanism is energetically favorable in such nanocrystalline coating/substrate systems as GaN/6H-SiC and AlN/6H-SiC systems in wide ranges of their parameters.

1. INTRODUCTION

Internal stresses are generated at interphase boundaries in thin solid films and thick coatings due to crystal lattice parameter mismatch, elastic modulus mismatch, thermal coefficient of expansion mismatch, and plastic flow mismatch between adjacent phases; see, e.g., [1-3]. Such stresses strongly or even crucially influence the integrity, structure, and properties of films and coatings. In particular, stress relaxation modes in single crystalline film/substrate systems often control their evolution during film growth [1,3]. In recent years, nanocrystalline coatings have become the subject of the rapidly growing scientific and technological interest because of their outstanding physical and mechanical properties different from those of coarse-grained coatings; see, e.g., [4,5]. The outstanding properties are treated to be caused by the nanocrystalline structure of such coatings. Also, one expects that, in parallel with the standard stress relaxation through formation of misfit dislocations at interphase boundaries, alternative stress relaxation mechanisms operate in nanocrystalline coatings due to their nanocrystalline structure. These expectations are supported by experimentally detected enhancement of stress relaxation in nanocrystalline coatings compared to their conventional coarse-grained counterparts. For instance, as it has been noted in paper [6], residual stresses are low in nanocrystalline cermet coatings (fabricated by thermal spray methods at highly non-equilibrium conditions), resulting in a capability for producing very thick coatings. So, nanocrystalline coatings were fabricated up to 0.65 cm thick and could probably be made with arbitrary thickness [6]. At the same time, in a conventional polycrystalline cermet coating, stress buildup limits coating thickness to typically 500-800 μm. This phenomenon is naturally explained as that caused by operation of special stress relaxation mechanisms which come into play in nanocrystalline coatings, but not conventional coarse-grained coatings. The main aim of this paper is to suggest and theoretically describe a special mechanism of stress relaxation in nanocrystalline coatings. The mechanism represents the local GB migration accompanied by formation of wedge disclination quadrupoles in nanocrystalline coatings.

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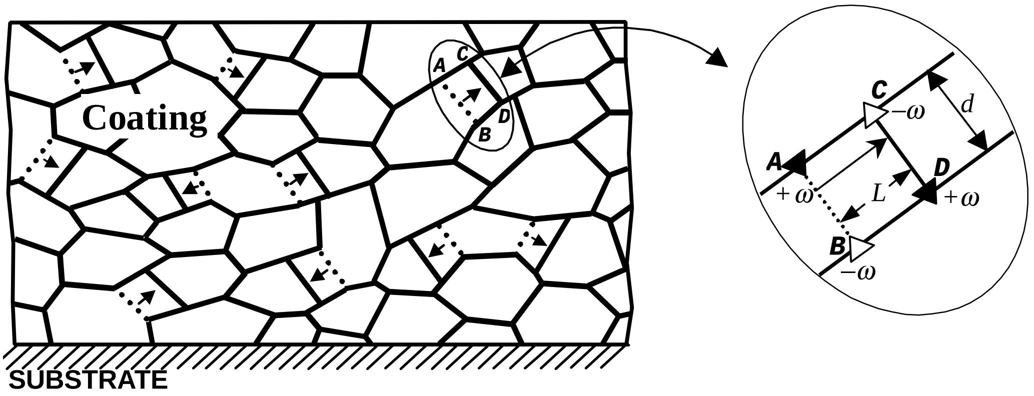

Fig 1. Athermal grain boundary migration is accompanied by formation of wedge disclination quadrupoles in nanocrystalline coatings. These quadrupoles serve as sources of stress fields compensating for, in part, mismatch stresses in nanocrystalline coatings.

2. ATHERMAL MIGRATION OF GRAIN BOUNDARIES AND FORMATION OF WEDGE DISCLINATION QUADRUPOLES IN NANOCRYSTALLINE COATINGS. MODEL

In general, stress relaxation in conventional solid films and coatings effectively occurs through plastic flow processes including, for instance, formation and slip of misfit dislocations. The latter deformation mode is a partial case of the standard lattice dislocation slip that dominates in conventional single crystalline and coarse-grained polycrystalline solids. At the same time, plastic flow in nanocrystalline solids is often realized through specific deformation mechanisms different from the standard lattice dislocation slip; see, e.g., reviews [7-10] and books [11,12]. The action of specific plastic deformation mechanisms is associated with the structural peculiarities of nanocrystalline solids where the volume fraction of the interfacial phase is extremely high, and grain size *d* does not exceed 100 nm. Besides the standard lattice dislocation slip, such deformation mechanisms as interfacial sliding, grain boundary diffusional creep (Coble creep) mode, twin deformation and rotational deformation are capable of essentially or even crucially contributing to plastic flow in nanocrystalline solids [7-12]. Recently, the athermal GB migration has been recognized as a special rotational deformation mechanism effectively operating in nanocrystalline solids [10,13-20]. In the context discussed, we think that the athermal GB migration can effectively contribute to stress relaxation in nanocrystalline coatings. More precisely, the athermal GB migration in nanocrystalline coatings, by analogy with bulk nanocrystalline materials [15], leads to the formation of wedge disclination quadrupoles (Fig. 1). These quadrupoles serve as stress sources capable of releasing, in part, mismatch stresses in nanocrystalline coatings.

In order to analyze in a first approximation the role of the athermal GB migration in stress relaxation in nanocrystalline coatings, we consider a model coating/substrate system containing a simply arranged ensemble of wedge disclination quadrupoles resulted from the athermal GB migration (Fig. 2). The system is composed of a semi-infinite substrate and a film of thickness *H* (Fig. 2). The substrate and film are assumed to be elastically isotropic solids having the same values of the shear modulus *G* and the same values of the Poisson' ratio ν. The coating/substrate boundary creates mismatch stresses. For definiteness, we consider the only crystal lattice parameter mismatch (misfit) characterized by one-dimensional misfit parameter $f = (a_f - a_s)/a_f$, where a_f and a_s are crystal lattice parameters of the coating and substrate, respectively. GB-migration-produced quadrupoles of wedge disclinations are assumed to be arranged periodically with period p (Fig. 2). All the disclination quadrupoles are supposed to be identical. The linear sizes of each quadrupole (distances between the disclinations composing of a quadrupole) are *L* and *d*. Since the disclination quadrupoles are

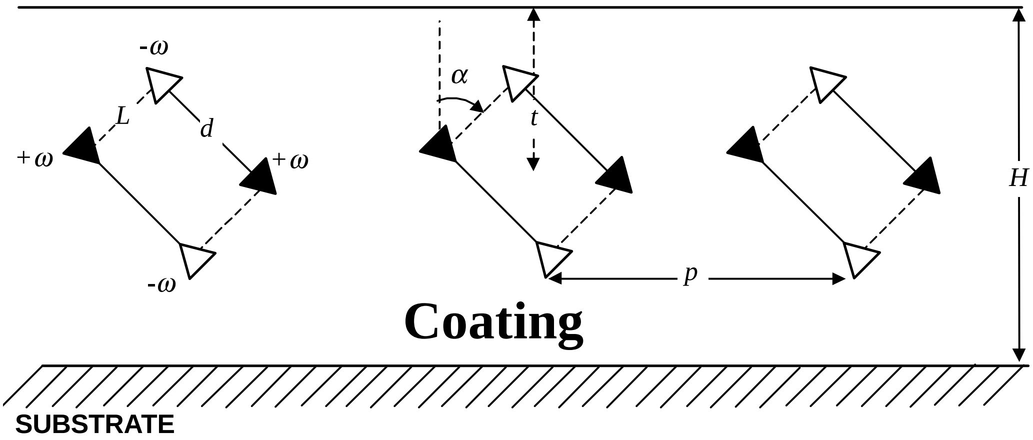

Fig 2. A model coating/substrate system with a periodically arranged row of identical wedge disclination quadrupoles (for details, see text).

formed due to GB migration (Fig. 1), the quadrupole size d is around the grain size. The disclination strengths are $\pm\omega$. The angle α characterizes orientation of each quadrupole relative to the coating/substrate boundary as shown in Fig. 2. The distance between the coating free surface and center of each quadrupole is t. Although this model arrangement of disclination quadrupoles (Fig. 2) is rather simple, it captures the essential physics of stress relaxation through athermal GB migration in real nanocrystalline coatings.

3. ENERGY CHARACTERISTICS OF WEDGE DISCLINATION QUADRUPOLES FORMED DUE TO GRAIN BOUNDARY MIGRATION IN NANOCRYSTALLINE COATINGS

Let us consider energy characteristics of the model ensemble of wedge disclination quadrupoles (Fig. 2) in a nanocrystalline coating/coating system. Formation of the wedge disclination quadrupoles due to the athermal GB migration in a nanocrystalline coating is characterized by the energy difference ΔW between the final (Fig. 2) and initial (defect-free) states. Formation of the wedge disclination quadrupoles is energetically favorable, if $\Delta W < 0$, and unfavorable otherwise.

The energy difference ΔW has the three terms:

$$\Delta W = E_{self}^{\Delta} + E_{\mathrm{int}}^{\Delta-f} + E_{\mathrm{int}}^{\Delta-\Delta}, \qquad (1)$$

where E_{self}^{Δ} is the proper energy of the row of the wedge disclination quadrupoles (Fig. 2); $E_{\mathrm{int}}^{\Delta-f}$ is the energy that characterizes the interaction between the disclination quadrupole row and the mismatch stresses, and $E_{\mathrm{int}}^{\Delta-\Delta}$ is the energy that characterizes the interaction between the disclination quadrupoles. The proper energy E_{self}^{Δ} of the wedge disclination quadrupoles can be written as the following sum of the proper energy of wedge disclination dipoles composing the quadrupoles and the energy of dipole-dipole interactions [21,22]:

$$E_{self}^{\Delta} = \frac{D\omega^2}{2p}\left(2L^2\cos^2\alpha + \frac{L^2}{2}\ln\frac{L^2\sin^2\alpha + 4t_1^2}{L^2} + \frac{L^2}{2}\ln\frac{L^2\sin^2\alpha + 4t_2^2}{L^2}\right) - D\omega^2\sum_{i=1}^{2}\sum_{j=3}^{4}(-1)^{i+j}\left(h_i h_j + \frac{l_{ij}^2 + (h_i - h_j)^2}{4}\ln\frac{l_{ij}^2 + (h_i - h_j)^2}{l_{ij}^2 + (h_i + h_j)^2}\right), \qquad (2)$$

where $D = G/[2\pi(1 - \nu)]$, $l_1 = L\cos\alpha$, $l_2 = L\sin\alpha$, $d_1 = d\cos\alpha$, $d_2 = d\sin\alpha$, $t_1 = t - d_2/2$, $t_2 = t + d_2/2$, $h_1 = t_1 - l_1/2$, $h_2 = t_1 + l_1/2$, $h_3 = t_2 - l_1/2$, $h_4 = t_2 + l_1/2$, $l_{13} = d_1$, $l_{14} = d_1 - l_2$, $l_{23} = d_1 + l_2$ and $l_{24} = d_1$.

The energy $E_{\mathrm{int}}^{\Delta-f}$ of the interaction between the disclination quadrupole row and the mismatch stresses is given by the standard expression [22]:

$$E_{\mathrm{int}}^{\Delta-f} = \frac{2\pi D}{p}(1+\nu)f\omega\left(h_2^2 - h_1^2 + h_3^2 - h_4^2\right). \qquad (3)$$

The energy $E_{\mathrm{int}}^{\Delta-\Delta}$ of the interaction between the disclination quadrupoles is calculated using the standard formula [21] that describes the energies of disclination-disclination interactions. In doing so, we find:

$$
\begin{aligned}
E_{\mathrm{int}}^{\Delta-\Delta} = \frac{D\omega^2}{p}\Bigg(&\frac{2\pi}{p}\left[\int_0^{h_1} h^2\coth\frac{2\pi h}{p}dh + \int_0^{h_2} h^2\coth\frac{2\pi h}{p}dh + \int_0^{h_3} h^2\coth\frac{2\pi h}{p}dh + \int_0^{h_4} h^2\coth\frac{2\pi h}{p}dh\right]\\
&-\frac{2\pi}{p+l_2}\left[\int_0^{h_1} h(h+l_1)\coth\frac{\pi(2h+l_1)}{p+l_2}dh + \int_0^{h_3} h(h+l_1)\coth\frac{\pi(2h+l_1)}{p+l_2}dh\right]\\
&-\frac{2\pi}{p+d_1}\left[\int_0^{h_1} h(h+d_2)\coth\frac{\pi(2h+d_2)}{p+d_1}dh + \int_0^{h_2} h(h+d_2)\coth\frac{\pi(2h+d_2)}{p+d_1}dh\right]\\
&-\frac{2\pi}{p-l_2}\int_0^{h_1} h(h+l_1)\coth\frac{\pi(2h+l_1)}{p+l_2}dh + \int_0^{h_3} h(h+l_1)\coth\frac{\pi(2h+l_1)}{p+l_2}dh\Bigg)\\
&-\frac{2\pi}{p-d_1}\left[\int_0^{h_1} h(h+d_2)\coth\frac{\pi(2h+d_2)}{p-d_1}dh + \int_0^{h_2} h(h+d_2)\coth\frac{\pi(2h+d_2)}{p-d_1}dh\right]\\
&+\frac{2\pi}{p+d_1-l_2}\int_0^{h_1} h(h+d_2+l_1)\coth\frac{\pi(2h+d_2+l_1)}{p+d_1-l_2}dh\\
&+\frac{2\pi}{p+d_1+l_2}\int_0^{h_2} h(h-d_2+l_1)\coth\frac{\pi(2h-d_2+l_1)}{p+d_1+l_2}dh\\
&+\frac{2\pi}{p-d_1+l_2}\int_0^{h_1} h(h+d_2+l_1)\coth\frac{\pi(2h-d_2+l_1)}{p-d_1+l_2}dh\\
&+\frac{2\pi}{p-d_1-l_2}\int_0^{h_1} h(h-d_2+l_1)\coth\frac{\pi(2h-d_2+l_1)}{p-d_1-l_2}dh.
\end{aligned}
\tag{4}
$$

Formulas (1)-(4) allow one to calculate the characteristic energy difference ΔW.

4. RESULTS OF MODEL CALCULATIONS IN EXEMPLARY CASES OF NANOCRYSTALLINE COATING/SUBSTRATE SYSTEMS GaN/6H-SiC AND ALN/6H-SiC

Let us use formulas (1)-(4) to calculate the characteristic energy difference ΔW in exemplary cases of scientifically and practically important nanocrystalline coating/substrate systems GaN/6H-SiC and AlN/6H-SiC. These systems are characterized by the following material parameters: G = 131 GPa, ν = 0.352 [23], f = -0.0357 [24], for GaN/6H-SiC; and G = 131 GPa, ν = 0.287 [23], f = 0.009 [25], for AlN/6H-SiC. With these material parameters and formulas (1)-(4), we calculated dependences of the energy difference ΔW on the angle α, for various values of the quadrupole size L and the following values of other parameters of the defect structure (Fig. 2): ω = 20°, p = 30 nm, H = 30 nm, $t = H/2$ and d = 10 nm. Fig. 3 presents dependences $\Delta W(\alpha)$, for L = 1 nm, 2 nm, and 3 nm. From Fig. 3 it follows that the most favorable direction of GB migration (leading to formation of a disclination quadrupole) makes angle $\alpha = \pi/4$ with a normal to the coating free surface. Also, note that, for angles α close to $\pi/4$, the energy profit ΔW increases with rising L in coating/substrate system GaN/6H-SiC (Fig. 3a). In the case of coating/substrate system AlN/6H-SiC, the energy profit ΔW decreases with rising L, for angles α close to $\pi/4$ (Fig. 3b).

With formulas (1)-(4) and the aforesaid values of parameters, we calculated dependences of the energy difference ΔW on the quadrupole size d (close to the grain size), for α = 45° and various values of the disclination strength magnitude: ω = 10°, ω = 20° and ω = 30°. These dependences are presented in Fig. 4 and show that formation of wedge disclination quadrupoles is energetically favorable (ΔW < 0) in

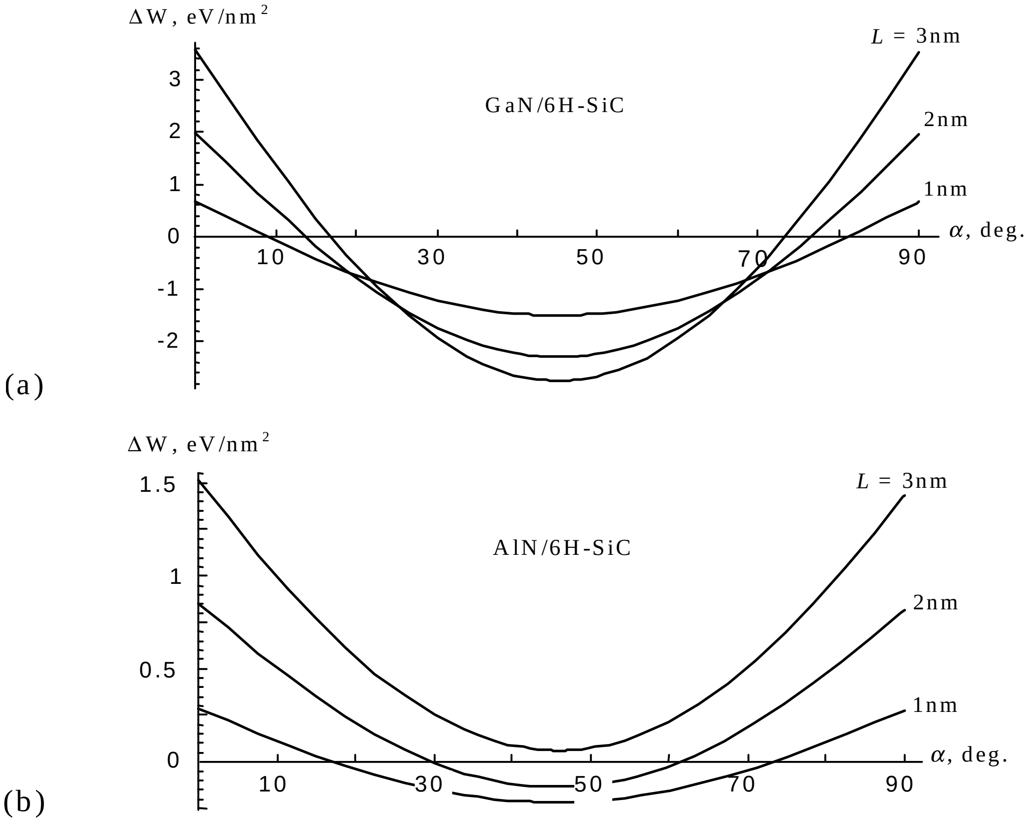

Fig 3. Dependences of the energy difference ΔW on the angle α (which specifies direction of grain boundary migration), for various values of the disclination quadrupole size L, in nanocrystalline coating/substrate systems (a) GaN/6H-Si and (b) AlN/6H-SiC.

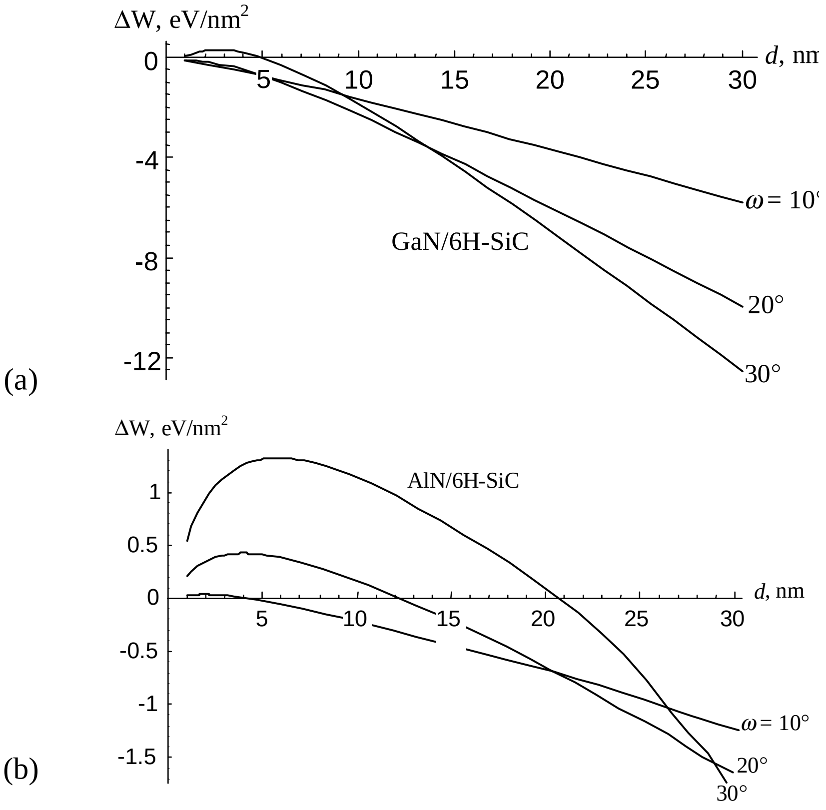

Fig 4. Dependences of the energy difference ΔW on the quadrupole size d (close to the grain size), for $\alpha = 45°$ and various values of the disclination strength magnitude ω, in nanocrystalline coating/substrate systems (a) GaN/6H-Si and (b) AlN/6H-SiC.

nanocrystalline coating/substrate systems GaN/6H-SiC and AlN/6H-SiC in wide ranges of their parameters.

5. CONCLUDING REMARKS

To summarize, results of our model calculations in exemplary cases of nanocrystalline coating/substrate systems GaN/6H-SiC and AlN/6H-SiC show that the athermal GB migration accompanied by formation of wedge disclination quadrupoles is energetically favorable in these systems in wide ranges of their parameters. This allows us to conclude that the athermal GB migration can serve as the special relaxation mechanism effectively releasing mismatch stresses in nanocrystalline coatings.

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