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# The confinement of phonon propagation in TiAlN/Ag multilayer coatings with anomalously low heat conductivity

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**Abstract**

TiAlN/Ag multilayer coatings with different number of bilayers and thicknesses of individual layers were fabricated by DC magnetron co-sputtering. Thermal conductivity was measured in dependence of Ag layer thickness. It was found anomalous low thermal conductivity of silver comparing to TiAlN and Ag bulk standards and TiAlN/TiN multilayers. The physical nature of such thermal barrier properties of the multilayer coatings was explained on base of reflection electron energy loss spectroscopy (REELS). The analysis shows that nanostructuring of the coating decreases the density of states (DOS) and velocity of acoustic phonons propagation. At the same time, multiphonon channels of heat propagation are degenerated. These results demonstrate that metal-dielectric interfaces in TiAlN/Ag coatings are insurmountable obstacles for acoustic phonons propagation.

**Keywords**: multilayer TiAlN/Ag PVD heterostructures, thermobarrier properties, phonon propagation, confinement, REELS

## Introduction

The “classic” thermal barrier coatings are based on several hundred micrometers oxide layers of Al, Zr, Y, and other elements that work as a passive protection of turbine blades surface or deal with streams of incandescent gases [1, 2]. These coatings do not use specific properties of nanoscale material. The raising attention in the last decade to micromechanical, micro- and nanoelectronical devices demands heat protection at such scale without increasing the overall dimensions. So, the solution of this antinomy could be found through specific properties of nanolaminate coatings based on metal-dielectric multilayers (MIM). These coatings pose an artificial heterogeneous phase nanocomposite whose physico-chemical properties differ drastically from those of its individual components due to size effects and corresponding sharp transformations of electronic structure of solids under such confinement [3]. The key feature of these metamaterials is their resonance response to external electromagnetic fields [4]. When an external electromagnetic irradiation interacts with these coatings, one can observe plasmon and phonon resonances corresponding to the source wavelength [5]. At the same time, these systems can be multifunctional as wear resistant coatings [5]. Abnormally low heat conductivity of MIM coatings [6, 7] opens good prospects in fields requiring heat protection of small units without significant changes of their dimensions. Most of predicted specific optical or electromagnetic properties of the planar metamaterials are based on anomalies in phonon and plasmon oscillations propagation [6].

It is well known that phonons are the main heat carriers in dielectric materials. The size-dependent changes in heat conductivity could rise when a characteristic size of a structural element comes comparable to phonon wavelength [7]. Also we can suppose that numerous interfaces between dissimilar materials provide a barrier for heat propagation due to Rayleigh scattering. In this way, increasing the number of interfaces could explain thermal barrier properties of heterogeneous phase materials [8]. In the other hand, the main heat transfer in metals occurs by collective oscillations of electrons in conduction band, i.e. plasmons. Previously, we assumed [6] that decreasing of degrees of freedom for electrons in thin 5 nm Cu layers sandwiched between TiAlN together with high number of metal-dielectric interfaces have led to anomalously low heat conductivity. The similar reduction of heat conductivity in multilayer dielectric films and nanostructured metals was reported also in [10 - 12]. It seems clear that heat conductivity of MIM coatings depends on features of propagation of both phonon and plasmon oscillations. This paper is aimed on study the size effect in phonon transport and heat transfer in TiAlN/Ag MIM coatings.

## Experimental

Multilayer $(Ti_{34}Al_{66})N/Ag$ heterostructures with different thicknesses of individual layers were fabricated by DC–magnetron co-sputtering on cemented carbide substrates. The thicknesses of individual layers were varied from several to several hundred nanometers. All samples were finished with a TiAlN overcoat to protect the silver layers from oxidation. Table 1 contains parameters of coatings that were used to investigate the difference between nanolayered and bulk coatings. Scanning transmission electron microscopy (STEM) was used to determine thicknesses and structure parameters of individual layers in deposited coatings. The cross-sectional specimen was prepared in a focused ion beam system (FEI Helios 600) by using the “in situ” lift-out technique. The lamella was thinned to electron transparency, first, with an acceleration voltage of 30 kV and, later, with 5 kV (for at least 2 min in each side) to minimize any possible preparation artifacts.

The electron spectroscopy investigations were carried out using multifunctional electron spectrometer ESCALAB MK2 (VG) equipped by EMU-50 source of monochromatic electrons ($E_0$ = 1 — 100 eV). The samples were cleaned by $Ar^+$ ions etching combined with XPS analysis for detection of sample surface purity. The same procedure was used for samples to denudate individual layers and the interface between TiAlN and Ag layers. The parameters of spectra acquisition were selected in the best way to provide high energy resolution of the specter full width at half maximum (FWHM) about 15 meV for high resolution reflected electron energy loss spectroscopy (HRREELS) investigations. Thermal conductivity of the as-deposited coatings was measured by a pulsed photothermal reflectance (PPR) technique described in details in [13].

## Results and Discussion

The STEM microphotograph on Figure 1a shows that the TiAlN/Ag coating had nanolaminate structure with perfect accommodation at the interfaces. This can be extracted from the propagation of the substrate roughness with the number of layers. This deposition mode points out to a nice conformal growth. This multilayer coating has 35 bilayers with uniform distribution of individual layers of 15 nm. The multilayer structure is well defined, with negligible intermixing and sharp interfaces.

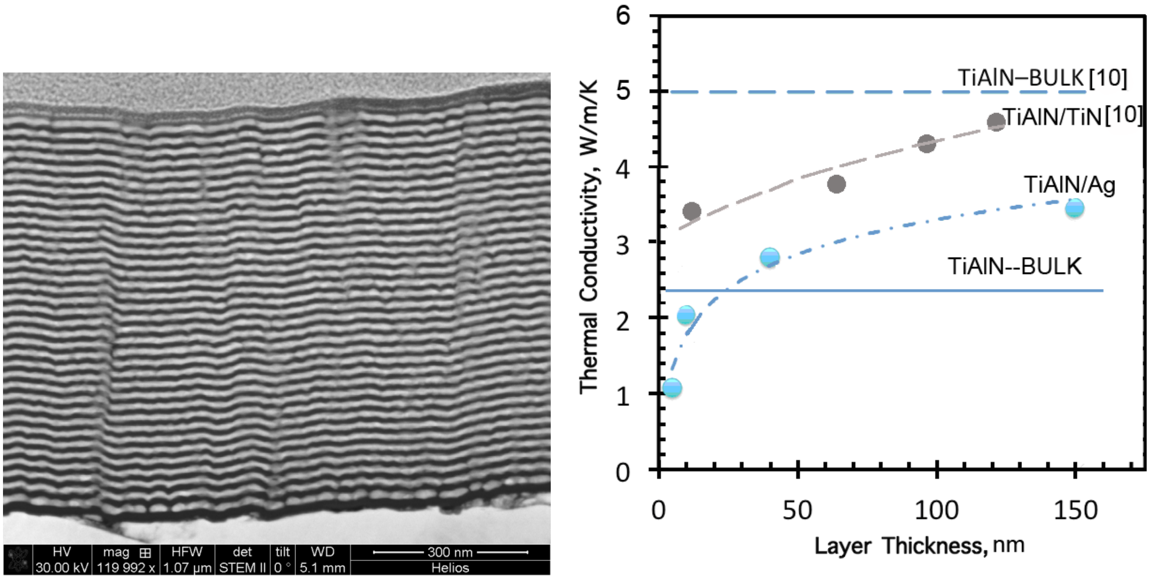


Figure 1. a – STEM cross-sectional image showing the structure of a TiAlN/Ag multilayer coating with 35 bilayers prepared by DC magnetron sputtering; b – The influence of the Ag film thickness on the thermal conductivity coefficient of TiAlN/Ag. These data are compared with literature ones for TiAlN/TiN coatings [10]

Thermal conductivity measurements were carried out on samples listed in Table 1, Ag bulk standard, and thick TiAlN coating (~1000 nm) prepared by DC-magnetron sputtering using the same targets.

Figure 1b demonstrates that thermal conductivity of the nanocomposite with Ag interlayers is extremely lower than for bulk Ag (480 $Wm^{-1}K^{-1}$). Moreover, according to the empirical dependence $K = 0.657\ln(t/t_0)$ ($Wm^{-1}K^{-1}$), the thermal conductivity of TiAlN/Ag composites with Ag layers thinner than 23.5 nm were also lower than of multilayer nitride TiAlN/TiN [10] plotted also on Fig. 1b for comparison. The MIM coating on base of TiAlN/Ag has lower thermal conductivity than TiAlN/TiN for wide range of layer thicknesses. It is very interesting result that the thermal conductivity of multilayer coatings significantly reduces with exchanging of TiN by a metal layer, Ag in our case. This phenomenon is most noticeable for layer thickness less than 30-20 nm.

Obviously, such sharp decreasing of thermal conductivity of the MIM nanocomposite with thickness of Ag layers less than 23.5 nm could be associated with a drastic transformation of the metal electronic structure due to size effects. Such reduction of conduction band electrons role in thermal conductivity of Ag should point out towards phonons as the major thermal transport mechanism. So, the investigation of their transport through the MIM structure and scattering at the interfaces becomes necessary for a more complete understanding of the observed anomalously low heat conductivity.

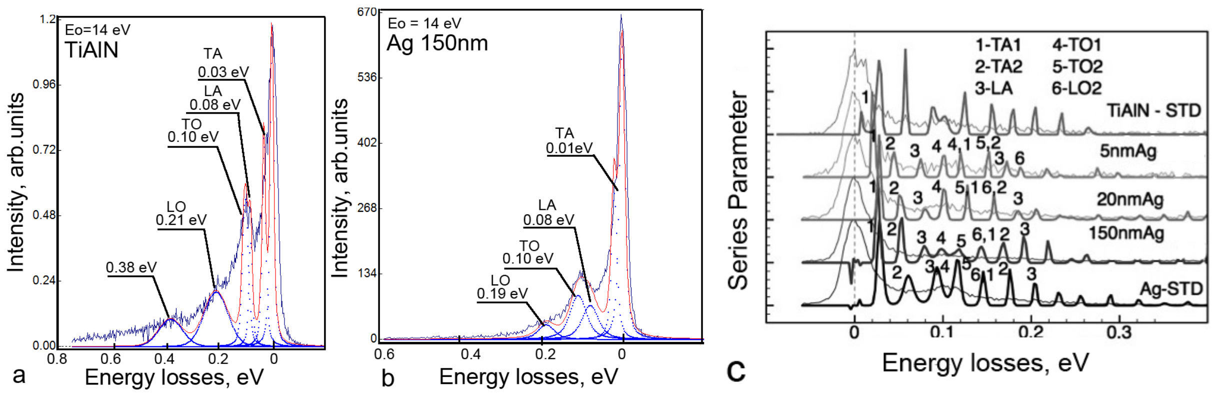


Figure 2. Experimental phonon spectra from TiAlN layer (a) and 150nm Ag layer (b) in multilayer coating; c - deconvolution of REELS for investigated specimens. Note that the scattering geometry employed in the present work corresponds to maximal intensity of phonon excitation ($E_0$ = 14 eV).

The original and deconvoluted vibrational (phonon) spectra from 1000nm TiAlN, Ag polycrystalline standard and MIMs with Ag layers of 5 nm, 20 nm and 150 nm are shown on Figure 2. One can see that experimental REELS spectra have complex structure, which contains acoustic (TA) and optical (TO) components. Deconvolution procedure allows estimating more precisely some finest changes of phonons energy with decreasing of Ag layer thickness. Silver has the face centered cubic (fcc) lattice with four atoms per unit cell. So we can observe not more than 3x4=12 modes of lattice vibrations: 3 acoustic and 9 optical modes. The first and second harmonics of longitudinal acoustic (LA) and optical (LO) phonon oscillations as well as transverse acoustic (TA) and optical (TO) ones are resolved after spectral deconvolution. One can see that the main spectral components positions are shifted with changing of Ag layers thickness.

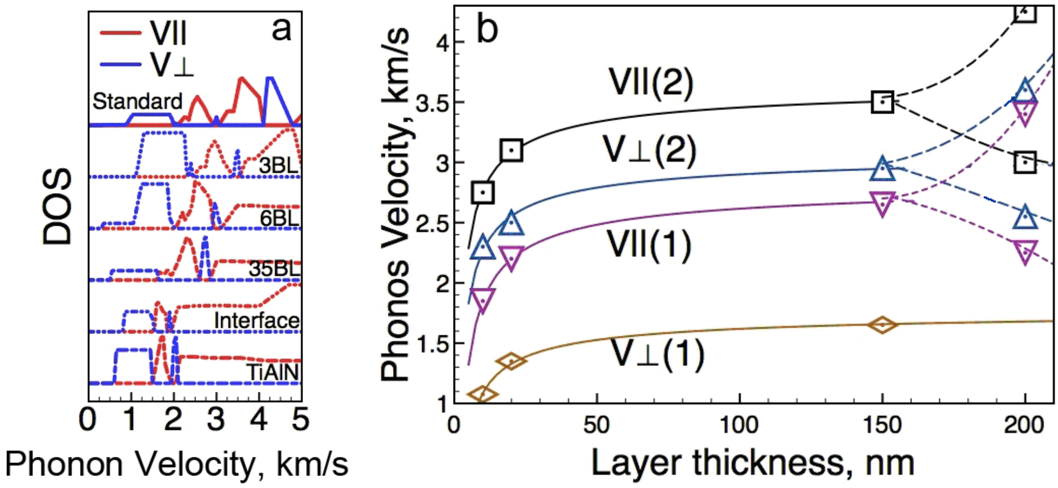


Figure 3. (a) Density of the states (DOS) of acoustic phonons and (b) dependence of Ag (TA) phonons velocity with Ag layer thickness in TiAlN/Ag coatings.

However, it is not only the energy of phonons that controls their propagation through the MIM. The density of phonons states, the direction of their propagation (parallel or perpendicular to layers) and their group velocity are also very important for understanding of heat transfer in MIMs. The analysis of these magnitudes is presented in Figure 3 and depicts the physical picture of the heat transfer by phonons in MIMs. Fig. 3-a demonstrates high DOS in Ag standard for a wide range of phonons velocities. Nanostructuring in multilayer coating shrinks the phonons spectrum and decreases their velocity. So, energy of acoustic phonons decreases together with the group velocity (speed of sound). It means that heat conductivity should lessen in nanostructured materials.

DOS of transversal phonon modes on the metal-dielectric interface that correspond to low velocities becomes lower with nanostructuring, so the interfaces are insurmountable obstacles for heat propagation by transversal phonons. Fig. 3-b shows phonons velocities in Ag layers with several thicknesses. We observe degeneration of phonons when the Ag layer thickness decreases below 150 nm: three upper branches with short and long components are gathering in points with equal velocity. This means that two-phonon processes are transformed into single-phonon ones at these points. So, heat transfer in Ag nanofilms is realized by phonon processes of low order. Phonon velocity is going down also. All these features mean that Ag layers thinning and increasing number of interfaces are attenuating the phonon contribution to heat conductivity in the coating.

The observed features of acoustic phonons spectra upon nanostructuring of Ag layers can be associated with a significant decline in the phonon mean free path due to the nanoscale size of the films (at least in the direction perpendicular to the substrate). This situation drastically influences on the phonons propagation behavior. First, the number of surface atoms becomes comparable to the volume atomic density and, in this case, it is necessary to take into account the system vibrations attributed to surface atoms. Second, phase incoherence at layer boundaries scatters and filters the phonon wave propagation and increases acoustic mismatch between the adjacent layers, hence, increasing the interfacial thermal resistance.

In addition, the periodic variation of the dielectric constant for the MIM nanocomposite creates forbidden states in the energy spectrum. This fact can radically affect the wave propagation in the infrared region. In some cases, this property is used for materials design with desired properties [14].

The interfaces cause coherent (elastic, Rayleigh) and incoherent (inelastic, Raman) scattering during heat propagation in the multilayer coating. This phenomenon depends on the structure and properties of the interfaces. This is even more critical for nanoscale systems where interfaces could significantly affect the properties in comparison to bulk materials [8]. Thus, one should expect a significant influence on the thermal conductivity by the interface quality of multilayer coatings.

## Conclusions

It was shown that the incorporation of  alternanating Ag layers with TiAlN causes a severe decrease in heat conductivity. This phenomenon is explained on the basis of several factors.

First of all, linear dimensions of the regions for the spatial localization of waves and quasiparticles in the transverse direction in nanolaminate materials become comparable to or less than their mean free path in the “infinite” bulk material.

Second, size effects results in the degeneration and quantization of the phonon spectrum, which significantly reduces the probability for each mode and, consequently, the energy transfer section of the wave in the direction given by the structural heterogeneity at the nanoscale. Third, the dimensionally constraint propagation of phonons in nanostructures reduces their phase space. This structural confinement decreases the transmission capacity of heat transfer by phonons.

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**References**


1. Y. Tamarin. Protective Coatings for Turbine Blades. ASM International, 2002
2. David R. Clarke, Matthias Oechsner, Nitin P. Padture. Thermal-barrier coatings for more efficient gas-turbine engines. MRS BULLETIN, Vol. 37( 2012), 891-898
3. K. Yao, Y. Liu, Plasmonic metamaterials, Nanotechnol. Rev. 3 (2014) 177–210.
4. J. Chen, G. Zhang, B. Li, Impacts of Atomistic Coating on Thermal Conductivity of Germanium Nanowires. Nano Lett. 12 (2012) 2826−2832.
5. X. Shen, T. J. Cui, Planar plasmonic metamaterial on a thin film with nearly zero thickness. Appl. Phys. Lett. 102 (2013) 211909.
6. A. I. Kovalev, D. L. Wainstein, A. Yu. Rashkovskiy, R. Gago, F. Soldera, J. L. Endrino, G. S. Fox-Rabinovich, Interface-Induced Plasmon Nonhomogeneity in Nanostructured Metal-Dielectric Planar Metamaterial. J. Nanomater. 2015 (2015) 876247.
7. A. Kovalev, D. Wainstein, A. Rashkovskiy, Investigation of anomalous physical properties of multilayer nanolaminate (TiAl)N/Cu coatings by electron spectroscopy techniques. Surf. and Interf. Anal. 42 (2010) 1361-1363.
8. R. M. Costescu, D. G. Cahill, F. H. Fabreguette, Z. A. Sechrist, S. M. George, Ultra-Low Thermal Conductivity in $W/Al_2O_3$ Nanolaminates. Science 303 (2004) 989-990.
9. G. Chen, R. Yang, X. Chen, Nanoscale heat transfer and thermal-electric energy conversion. J. Phys. IV France 125 (2005) pp. 499-504.
10. M.K. Samani, X.Z. Ding, N. Khosravian, B. Amin-Ahmadi, Y. Yi, G. Chen, E.C. Neyts, A. Bogaerts, B.K. Tay, Thermal conductivity of titanium nitride/titanium aluminum nitride multilayer coatings deposited by lateral rotating cathode arc, Thin Solid Films 578 (2015) 133–138.
11. Z. Cheng, L. Liu, S. Xu, M. Lu, X. Wang, Temperature Dependence of Electrical and Thermal Conduction in Single Silver Nanowire, Scientific Reports 10718 (2015).
12. X. Wang, K. D. Parrish, J. A. Malen, P. K. L. Chan. Modifying the thermal conductivity of small molecule organic semiconductor thin films with metal nanoparticles, Scientific Reports 16095 (2015)
13. D. G. Cahill, Analysis of heat flow in layered structures for time-domain thermoreflectance, Rev. Sci. Instrum. 75 (2004) 5119-5122.
14. T. Gorishnyy, M. Maldovan, C. Ullal, E. Thomas, Sound ideas. Phys. World; 2005, *18* (12), pp. 24–29.

**Figures captions**

Figure 1 a–Structure of TiAlN/Ag multilayer coatings with 35 bilayers prepared by DC magnetron sputtering; b – The influence of the Ag film thickness on the thermal conductivity coefficient of TiAlN/Ag. These data are compared with literature ones for TiAlN/TiN coatings [10]

Figure 2 Experimental phonon spectra from TiAlN layer (a) and 150 nm Ag layer (b) in multilayer coating c- Results of the deconvolution of REELS for investigated specimens. Note that the scattering geometry employed in the present work corresponds to maximal intensity of phonon excitation ($E_0$ =14 eV).

Figure 3 Density of the states (DOS) of acoustic phonons (a) and dependence of Ag (TA)-phonons velocity from layer thickness in TiAlN/Ag coatings (b)

Table 1 – Multilayer coatings composition parameters

| Sample's Symbol | TiAlN single layer thickness, nm | Ag single layer thickness, nm | Number of TiAlN/Ag bilayers | Total Thickness, nm |
|---|---|---|---|---|
| 3BL | 150 | 150 | 3+150nm TiAlN above | 1050 |
| 6BL | 150 | 20 | 6+150nm TiAlN above | 1170 |
| 6BL+100 | 40 | 40 | 6+100nm TiAlN below | 580 |
| 35BL | 15 | 15 | 35+15nm TiAlN above | 1065 |