Functional Materials 12, No.1 (2005)

Optical properties of TiAlSiN based thin films

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Spectroellipsometric investigations of optical properties of TiAlSiN based thin films have been performed. The dispersive dependences of the film optical conductivity σ have been obtained in the 1–5 eV spectral range. The observed intense absorption in the near ultraviolet range and some low intensity peculiarities in the near infrared one against a background of intraband absorption in the σ curves are related to the interband electron transitions. The character differences in σ curves for various coatings could be explained by different chemical composition and the deposition techniques.

Проведены спектроэллипсометрические исследования оптических свойств тонких пленок на основе TiAlSiN. Получены дисперсионные зависимости оптической проводимости σ покрытий в спектральном интервале 1–5 эВ. Интенсивное поглощение в ближней ультрафиолетовой спектральной области и малоинтенсивные особенности в ближней инфракрасной области на фоне внутризонного поглощения, которые наблюдаются на кривых σ, связаны с междузонными переходами электронов. Отличия в характере кривых σ для различных покрытий можно объяснить различными химическими составами, а также способами их напыления.

Since many years, the TiN family of materials has been used as hard, wear-resistant coatings for cutting and drilling tools working in hard conditions to enhance the tool service time [1–3]. Many efforts have been undertaken to improve the high temperature oxidation resistance and hardness of TiN coatings by optimising the PVD deposition parameters. The addition of ternary elements, particularly aluminium, enhances the oxidation resistance and the hardness [4]. Moreover, Al favors the grain refinement [5], although the $Ti_{1-x}Al_xN$ coatings retain the TiN crystallographic structure. Lee et al. showed that the single-phase TiN structure was maintained for a composition ratio up to $x = Al/(Al + Ti) = 0.8$, however, the hardness and adhesion of the films decrease as the Al content goes beyond the values of $x = 0.12$ [6].

The effect of Al and Si addition on physical and mechanical properties of TiN was investigated comprehensively by Vaz et al. [7]. Both elements enhance the oxidation resistance and the adhesion behaviour of the films. Additionally, Si in TiSiN nanocomposites improves considerably their hardness [8]. Unfortunately, the optical properties of such materials are not studied enough. Here, we present the investigations of optical conductivity of TiSiN based thin films.

Studied were TiAlN and TiAlSiN films of about 2 μm thickness deposited on WC-Co substrates using arc plasma PVD technique [9], single-layer (SL) Ti-rich and Al-rich thin films, gradient nanocomposite (GNC), and multilayer (ML) materials from PLATIT® AG (Grenchen, Switzerland). In GNC coating, Al content decreases continuously along the sample cross section from the surface to the substrate, while Ti-rich zone being closer to the substrate. The chemical composition of the thin films was analysed by Rutherford backscattering spectroscopy (RBS) and particle-induced X-ray emission (PIXE) using a 2 MeV proton beam and a 2 MeV He^+ beam, respectively (CAFI, LeLocle, Switzerland). The optical characteristics of coatings have been measured at fixed

Table 1. Chemical composition, thickness, and hardness as measured by NanoIndenter XP® system

#	Chemical composition	t, μm	H, GPa
1	$Ti_{34}Al_{14}Si_1N_{51}$ (SL)	0.88	38.6
2	$Ti_{14}Al_{28}Si_4N_{57}$ (SL)	1.58	34.5
3	$Ti_{22}Al_{24}Si_2N_{52}$ (GNC)	2.05	29.4
4	$Ti_{26}Al_{25}Si_3N_{46}$ (ML)	2.15	33.5

light incidence angle $\varphi = 72°$ in spectral range $h\nu = 1$ to 5 eV using spectroellipsometric Beattie method. The light intensity passed through system of polarizer-specimen-analyzer was measured at three fixed azimuths of the analyzer $\Psi_A = 0$, 45, 90° and fixed azimuth of the polarizer $\Psi_P = 45°$ to define the ellipsometric parameters Δ (phase shift between the orthogonal components of the polarization vector) and Ψ (azimuth of the restored linear polarization). The determination accuracy of ellipsometric parameters was not worse than 3 to 5 %. Basing on those parameters, the effective refraction n and absorption k indices, and the optical conductivity $\sigma(h\nu) = nk\nu$ were determined (ν is the light frequency). The model of semi-infinite medium was used to calculate n and k, since the investigated thin films are non-transparent in visible, near infrared (IR), and ultra-violet (UV) spectral ranges.

The overall chemical composition of the investigated thin films is summarized in Table.

The following remarks concerning the analysis can be made:

1. It is very difficult to determine the ratio between Al and Si using RBS. The total concentration of Al and Si is more accurate than the individual values.

2. The uncertainty in the Ti concentration is about 1 at. %, the uncertainty in the Al + Si concentration, is about 2 at. %, that in the N concentration, about 3 at. %.

The X-ray diffraction examination [10] shows broad diffraction peaks typical of nanocrystalline structure. In the Al-rich SL TiAlN sample (#2), the typical phases are *fcc*-AlN and a small amount of *fcc*-TiN. Increasing in Ti content (samples ##1, 3, and 4) results in formation of *fcc*-Ti_3AlN accompanied by disappearance of the AlN phase. The integral intensity of the Ti_3AlN peaks increases and their widths decrease with increasing Ti-content, which corresponds to

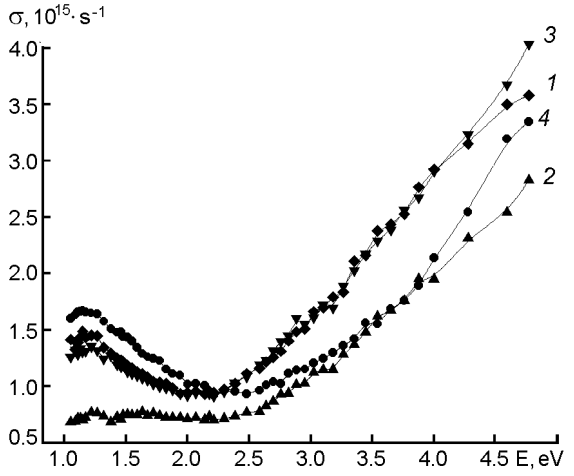

Fig. Optical conductivity spectra of TiAlSiN based thin films: $Ti_{34}Al_{14}Si_1N_{51}$ (*1*), $Ti_{14}Al_{28}Si_4N_{57}$ (*2*), $Ti_{22}Al_{24}Si_2N_{52}$ (*3*), $Ti_{26}Al_{25}Si_3N_{46}$ (*4*).

increased crystalline volume fraction and decreased average crystallite size. The formed phases are in accordance with Haegg rules [11].

The dispersive dependences of the coating optical conductivity σ in the experimental spectral range are shown in Fig. 1. The main features of all presented $\sigma(E)$ curves (E is the photon energy) are the presence of a minimum in visible range at $E = 2$–2.5 eV and an essential absorption in the near UV range. Some low intensity peculiarities are also observed in the near IR range against a background of intraband absorption which are related to the interband electron transition. The σ values for sample # 2 are as low as a half of the others in this range. It is to note that $\sigma(E)$ behavior is almost the same for samples # 1 and # 3. So, the subsurface layer with gradient distribution of Ti and Al does not change its optical properties. The character of $\sigma(E)$ curve for sample # 4 differs from those of ## 1, 3. In particular, the minimum in $\sigma(E)$ dependence is shifted towards higher photon energies. As the depth of light penetration into the subsurface layer (the skin-layer thickness is d_s ~ 20 nm) decreases with the shortening of wavelength, it becomes comparable to the thickness of similar layers for TiN and Ti_3AlN (d_{TiN} ~ 5–6 nm, $d_{Ti3}AlN$ ~ 8–10 nm, respectively). So, one can conclude that the origin of such shift is in the different chemical composition.

Let the features of σ(E) curves be considered in more detail. The model of interband absorption in single-electron approach is developed on the base of direct and indirect

transitions. The model of indirect transitions, namely, the Berglung-Spicer model [12] is used to describe the frequency dispersion of dielectric permeability in disordered metal medium. In this approach, the contribution of electron transitions from filled i band to free j band to optical conductivity is defined by state density thereof:

$$\sigma_{ij}(\hbar\omega) = \frac{1}{\hbar\omega} \int_{E_F}^{E_F + \hbar\omega} W_{ij} N_i(E' - \hbar\omega) N_j(E') dE', \quad (1)$$

where E' is the electron binding energy; W_{ij}, the transition matrix element (transition probability) from the initial i stage to the final j one.

According to the X-ray diffraction data [10], TiN, AlN, Ti_3AlN phases are present in the investigated thin films. Theoretical considerations of binding structure and energy spectrum of the electron state density show that in TiN, the allowed electron transitions are $(\Gamma'_{25} - \Gamma_{12})$ between hybridized $3d(2p) \rightarrow 3d(2p)$ states at $E = 1.3$ eV [13]. However, for TiN compound, the intraband absorption mechanism in the near IR range becomes dominant over the mechanism of quantum interband electron transitions. In particular, in [14], the optical conductivity decreases monotonously in the range of 1 to 2 eV with energy of probe photons and no peculiarities at $E = 1.3$ eV are observed.

Aluminum nitride is an unalloyed wide band semiconductor ($E_g \approx 6$ eV). So, the interband absorption in the IR range is always absent and the first low-energy maximum in $\sigma(E)$ spectrum is observed at $E = 2.8$ eV [15] and is generated due to involving of the electronic states connected to the nitride vacancies into the quantum absorption. The mentioned feature is also observed for all samples at $E = 2.8$–3.2 eV. So, it is possible that the peculiarities of $\sigma(E)$ experimental curves in the near IR range could be related to the interband electron transitions in Ti_3AlN which is formed in the subsurface layer.

At the same time, the decreasing of intraband absorption for the sample # 2 in near IR range could be caused by the following. First, the mentioned thin film could exhibit a higher disordering extent which results in an increased scattering intensity of charge carriers, so, a decreased contribution of intraband transitions into optical conductivity. Second, the increase of AlN phase volume fraction and decrease TiN phase one takes place and, as it was mentioned above, the intraband absorption in IR range is always absent in AlN.

To conclude, optical conductivity of single layer, multilayer, and gradient nanocomposite TiAlSiN thin films have been studied. The dispersive dependences of optical conductivity σ of the coatings have been obtained in spectral range 1–5 eV. The observed substantial absorption in the near ultra-violet range and some low intensity peculiarities in the near infra-red range against a background of intraband absorption in the σ curves are related to the interband electron transitions. The differences in character of σ curves for various coatings could be explained by different chemical composition and deposition techniques. More detailed studies are required to understand completely all observed peculiarities in the optical conductivity spectrum.

Acknowledgements. The authors would like to thank Dr.M.Morstein for producing samples and Drs.S.Mikhailov and F.Munnik (CAFI-EICN, Le Locle, Switzerland) for providing RBS measurements.

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Оптичні властивості тонких плівок на основі TiAlSiN

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Проведено спектроеліпсометричні дослідження оптичних властивостей тонких плівок на основі TiAlSiN. Отримано дисперсійні залежності оптичної провідності σ покриттів у спектральному інтервалі 1–5 еВ. Інтенсивне поглинання у ближній ультрафіолетовій спектральній області та малоінтенсивні особливості у ближній інфрачервоній області на фоні внутрішньозонного поглинання, які спостерігаються на кривих σ, пов'язані з міжзонними переходами електронів. Відмінності у характері кривих σ для різних покриттів можна пояснити різними хімічними складами, а також способами їх напилення.