Solar Energy Materials & Solar Cells 92 (2008) 1425–1433

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Optical properties and thermal stability of TiAlN/AlON tandem absorber prepared by reactive DC/RF magnetron sputtering

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ARTICLE INFO

Article history:
Received 28 March 2008
Accepted 4 June 2008
Available online 18 July 2008

Keywords:
Tandem absorber
Titanium aluminum nitride
Aluminum oxynitride
Optical properties
Sputtering

ABSTRACT

Spectrally selective TiAlN/AlON tandem absorbers were deposited on copper and stainless steel substrates using a reactive DC/RF magnetron sputtering system. The compositions and thicknesses of the individual component layers were optimized to achieve high absorptance ($\alpha = 0.931$–0.942) and low emittance ($\varepsilon = 0.05$–0.06) on copper substrate. The experimental spectroscopic ellipsometric data have been fitted with the theoretical models to derive the dispersion of the optical constants (n and k). In order to study the thermal stability of the tandem absorbers, they were subjected to heat treatment (in air and vacuum) for different durations and temperatures. The tandem absorber deposited on Cu substrates exhibited high solar selectivity (α/ε) of 0.946/0.07 even after heat treatment in air up to 600 °C for 2 h. At 625 °C, the solar selectivity decreased significantly on Cu substrates (e.g., $\alpha/\varepsilon = 0.924/0.30$). The tandem absorber on Cu substrates was also stable in air up to 100 h at 400 °C with a solar selectivity of 0.919/0.06. Studies on the accelerated aging tests indicated that the activation energy for the degradation of the tandem absorber is of the order of 100 kJ/mol.

1. Introduction

A good selective absorber is characterized by a high absorptance (α) in the wavelength range of 0.3–2.5 μm and a low emittance (ε) at higher operating temperatures [1]. The efficiency of photothermal conversion at high temperatures strongly depends on the optical properties and thermal stability of the component materials used in the solar absorbers. Various concepts such as absorber–reflector tandem, cermet coatings and multilayer absorbers have been used by several authors in order to achieve efficient photothermal conversion [2–6]. Among these, the absorber–reflector tandem concept has been utilized extensively to achieve high spectral selectivity [1].

Generally, copper is used as the substrate for solar selective absorbers because copper has high thermal conductivity, low resistivity and high infrared reflectance. But, at temperatures greater than 300 °C, copper gets oxidized and diffuses into the absorber layer, resulting in degradation of the solar selective absorbers. A diffusion barrier layer with high thermal stability and good optical properties can prevent the diffusion of Cu into the absorber layer. In recent years, transition metal nitrides like TiAlN have been used as diffusion barriers for copper metallization in micro-electronic devices and packaging applications [7]. TiAlN coatings exhibit high thermal stability, chemical inertness and low electrical resistivity at higher temperatures [7,8]. Although TiAlN films were initially developed for hard coating applications due to their high hardness, low friction coefficient and excellent oxidation resistance at higher temperatures [9], they have also attracted attention for the fabrication of complementary metal-oxide semiconductor memory devices [10]. Similarly, aluminum oxynitride thin films (AlO_xN_y) are also widely used as optical and protective coatings, diffusion and corrosion in research areas such as microelectronics and optoelectronics [11–13]. The mechanical properties of AlON films prepared using sputtering of Al_2O_3 in $Ar+N_2$ plasma have been studied by various authors [14,15]. It has been reported that these coatings exhibit hardness as high as 13 GPa.

The optical properties (α, ε) of TiAlN and AlON have scarcely been investigated [11–13,16]. It has been reported that single-layer TiAlN coatings show an absorptance of 0.8 [16]. The optical properties of 'Ti' based nitride coatings can be tailored by controlling the stoichiometry, which affects the density of free electrons in the Ti 'd' band [16,17]. Incorporation of additional element (such as Al) in the TiN matrix changes the bonding structure (e.g., metallic to covalent). It is known that TiN exhibits metallic character and AlN exhibits covalent character. The change in the bonding structure results in variations in the electrical resistivity and the optical properties of TiAlN. The physical properties of AlON thin films can also be tailored between that of AlN and Al_2O_3. AlN has high electrical resistivity (~10^{14} Ω cm), very high thermal conductivity (180 W/m K at 25 °C) and moderately low dielectric constant (8.8 at 1 MHz) [18]. The refractive

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doi:10.1016/j.solmat.2008.06.004

index of AlN coating was found to be in the range of 1.94–2.11 in the wavelength region of 300–1200 nm [19]. Al_2O_3 has high electrical resistivity, high chemical stability, high hardness, etc. and the refractive index of Al_2O_3 is in the range of 1.5–1.9 in the wavelength range of 300–1200 nm [12,20]. The characteristics of both AlN and Al_2O_3 can be combined in a single AlON film by varying the amount of Al, N and O.

In this paper, we present the optical properties (α and ε) of TiAlN/AlON tandem absorber heat-treated (in air and vacuum) at different temperatures and durations. Solar spectrum reflectometer, emissometer, atomic force microscopy (AFM), phase-modulated spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS) and micro-Raman spectroscopy techniques have been used to characterize the tandem absorbers. Accelerated aging tests have also been performed on these coatings.

2. Experimental details

TiAlN/AlON tandem absorbers were deposited on Cu (dimensions: $0.035 \times 0.035 \times 0.002$ m) and stainless steel substrates using reactive DC/RF magnetron sputtering system that has been described in detail elsewhere [21]. The sputtering guns (diameter = 0.075 m) had planar magnetron geometry. The substrate to sputtering target distance was 0.054 m. High-purity Ti–Al (99.95%) and Al_2O_3 (99.999%) targets were used for the deposition of the coatings. The composition of the Ti–Al target was approximately 50:50 at%. Before putting the substrates into the vacuum chamber, the substrates were metallographically polished and chemically cleaned in an ultrasonic agitator in acetone, absolute alcohol and trichloroethylene. The vacuum chamber was pumped down to a base pressure of 5.0×10^{-4} Pa. The substrates were cleaned in situ by argon ion bombardment for 30 min, wherein a DC bias of −850 V was applied to the substrate at an argon pressure of 6.0×10^{-1} Pa. A DC power supply was used to deposit TiAlN layer and an RF power supply (frequency = 13.56 MHz) was used to deposit the AlON layer. Sputtering was carried out at power densities of 5.0 and 6.8 W/cm^2 for TiAlN and AlON coatings, respectively. TiAlN coating was prepared from the reactive sputtering of Ti–Al composite target in argon–nitrogen plasma at a pressure of 1.0×10^{-1} Pa and the nitrogen flow rate was varied from 1 to 3 sccm. AlON coating was deposited using the Al_2O_3 target in argon–nitrogen plasma at a pressure of 1.0×10^{-1} Pa. For AlON deposition, the nitrogen flow rate was varied from 1 to 2.5 sccm.

The tandem absorber consists of two absorber layers with different metal volume fractions and different layer thicknesses. The first absorber layer TiAlN has a higher metal volume fraction than the second absorber layer AlON. These tandem absorbers are strongly absorbing in the visible region and transparent in the thermal IR region, which results in high absorptance and low thermal emittance.

The total hemispherical absorptance and total hemispherical emittance of the tandem absorber were measured using solar spectrum reflectometer and emissometer (M/s. Devices and Services). The absorptance of the coatings was measured at room temperature. For the solar spectrum reflectometer, the source of the illumination was a tungsten-halogen lamp. The radiation reflected by the sample was measured at an angle of 20° from the normal, with four filtered detectors (UV, blue, red and infrared). By summing the four outputs in the appropriated proportions, a solar spectrum measurement was achieved. Air mass 2 was used to calibrate the solar reflectometer. This emissometer is a special purpose instrument to measure the total hemispherical emittance of absorber coatings used for flat plate solar thermal collector, wherein the maximum working temperature of the collector is of the order of 80–85 °C. The detector in the emissometer consists of a differential thermopile with low and high emittance areas, which ensures near constant response to the emitted radiation in this wavelength range. The instrument was calibrated using standard samples. The accuracies of the measured α values are $\pm 2\%$ with a drift of $1\% + 0.003\,h^{-1}$ and the emissometer has a repeatability of ± 0.01 units. The absorptance and the emittance values were measured at four different positions and the values reported herein are the average of four measurements. The optical constants (n and k) of individual layers of the tandem absorber were measured in a phase-modulated spectroscopic ellipsometer (UVISEL™ 460, ISA JOBIN-YVON SPEX) in the wavelength range of 300–1200 nm.

The bonding structure of the coatings was characterized by XPS using an ESCA 3000 (V.G. Microtech) system with a monochromatic Al Kα X-ray beam (energy = 1486.5 eV and power = 150 W). The partial pressures of H_2O and O_2 in the deposition chamber were measured using an Accu Quad-100D residual gas analyzer (RGA). Surface imaging of the as-deposited and heat-treated samples was carried out using AFM (Surface Imaging Systems). The maximum scan ranges for AFM in the X-, Y- and Z-axes were 40, 40 and 4 μm, respectively. The AFM resolution along the X-, Y- and Z-axes was <1 nm. The AFM was operated in contact mode.

In order to test the thermal stability, the TiAlN/AlON tandem absorber deposited on copper and stainless steel substrates was heated in air in a resistive furnace at temperatures in the range of 400–900 °C for 2 h. Annealing involved increasing the temperature of the samples from room temperature to the desired temperature at a slow heating rate of 3 °C/min and maintaining the desired temperature for 2 h. Subsequently, the samples were cooled down at a rate of 3 °C/min. Thermal stability of the coatings in vacuum (5.0×10^{-4} Pa) was also studied. Accelerated aging tests have been carried out to evaluate the performance of the coatings. Changes as a result of the heating were measured using micro-Raman spectroscopy and AFM. A DILOR-JOBIN-YVON-SPEX integrated micro-Raman spectrometer was used for the present study.

3. Results and discussion

The process parameters such as target power density, N_2 flow rate and layer thicknesses were optimized in order to obtain a TiAlN/AlON tandem absorber with high absorptance and low emittance. Absorptance in the range of 0.931–0.942 and an emittance of 0.05–0.06 were obtained for the optimized process parameters listed in Table 1. The absorptance and the emittance

Table 1
Optimized process parameters for the deposition of TiAlN/AlON tandem absorber deposited on copper substrates

Layer	N_2 flow rate (sccm)	Power (W)	Thickness (nm)	Substrate temperature (°C)	Operating pressure (Pa)
TiAlN	2.5	225 (DC)	62	40	1.0×10^{-1}
AlON	2.0	400 (RF)	92	40	1.0×10^{-1}