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Spectral radiative properties of tungsten thin films in the infrared

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ABSTRACT

Tungsten is an important material for energy harvesting applications due to its high chemical and thermal stability; however, the difficulty in obtaining single-crystal films leads to a large variation in the optical properties. The present work focuses on the radiative and optical properties of thin tungsten films at wavelengths from 1 to 20 μm (wavenumbers from 10,000 to 500 cm^{-1}), considering microstructural variations. Four films of a nominal thickness of 70 nm were deposited on silicon substrates using DC magnetron sputtering, and the effect of pre- and post-deposition treatments was investigated. Several analytical instruments were used to characterize the crystalline phases and microstructures, including X-ray diffraction, Rutherford backscattering, X-ray photoelectron spectroscopy, and scanning electron microscopy. The transmittance and reflectance of the film–substrate composites were measured at room temperature using a Fourier-transform infrared spectrometer. The dielectric function of each sample was obtained by fitting the measured radiative properties using the Drude–Lorentz dispersion model. The difference in the radiative properties between samples was analyzed and related to the crystalline phases and density.

1. Introduction

Tungsten has been used as a high-temperature thermal emission source because of its good thermal and chemical stability with a melting temperature near 3400 °C [1–4]. Tungsten thin films allow for a reliable, high-temperature emission source integrated into a nanofabricated package. Tungsten gratings or microcavities [5–8], photonic crystals [9–11], thin-film multilayers [10], and hybrid micro/nanostructures [12] have recently been proposed as thermal emission sources for energy harvesting applications including thermophotovoltaic power generation. While some use tungsten films as a thermal emission source and others use them as a metal layer, knowledge of the optical properties is required for all applications. Therefore, it is critically important to understand the optical and radiative properties of tungsten, particularly in relation to the effect of microstructures.

Earlier, De Vos [2] measured the spectral emissivity of bulk single-crystal tungsten from 0.23 to 2.7 μm at temperatures from 1600 to 2800 K. Larrabee [3] reported the spectral emissivity of tungsten in a similar temperature range up to 5 μm, considering the effects of polarization for various emission angles, and the optical constants (i.e., complex refractive index) of tungsten were obtained. The total hemispherical emissivity of tungsten was also measured using a calorimetric technique [4]. Roberts et al. [13] postulated a superposition formula that includes a summation of Drude terms and Lorentz terms to obtain the optical constants of tungsten based on the reflectance measurements in the wavelength region from 0.365 to 2.56 μm. Nomerovannaya et al. [14] determined the dielectric function from 0.265 to 20 μm using one Drude term and several additional Lorentz terms to describe the interband transitions. These interband absorption mechanisms have been validated through theoretical energy-band calculations [15,16].

Weaver et al. [17] presented the dielectric function of tungsten from 0.15 to 33 eV using the Kramers–Kronig relation based on the absorptance (0.15–4.4 eV) and reflectance (4–33 eV) measurements. Additional high-energy data were used from another study along with an extrapolation. A Drude term was used to extend the optical properties to the far-infrared region beyond 8.3 μm wavelength [17]. The room-temperature optical constants of crystalline bulk tungsten were compiled by Palik [18], which is based on the results from Weaver et al. [17] from the ultraviolet to the far-infrared. Rakić et al. [19] used an optimization procedure to fit the data presented in Ref. [18] with an optical dispersion that includes contributions from both free and bound charges. The parameterized formulation can capture the fundamental physics and facilitate numerical simulations using a smooth curve without the need of interpolation from discrete data points. Very few studies dealt with the optical properties of tungsten thin films, which can have very different characteristics compared with single-crystal tungsten [20–23].

Deineka et al. [20] used spectral ellipsometry in the visible to near-infrared region to study ultrathin (2–8 nm) tungsten films

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Nomenclature

d	thickness, m
i	$\sqrt{-1}$
M	number of Lorentz oscillators
m^*	effective mass, kg
m_e	rest mass of an electron, kg
N	number of data points
$\tilde{n}$	complex refractive index
n	refractive index
n_e	carrier concentration, m^{-3}
R	reflectance
T	transmittance

Greek symbol

α_1, α_2, α_3	weighting coefficients
Γ	scattering rate in the Drude term, rad/s (1 rad/s = 5.31×10^{-12} cm^{-1})
γ	scattering rate or damping coefficient in the Lorentz term, rad/s
δ	penetration depth, m
$\tilde{\varepsilon}$	complex dielectric function ($\varepsilon_1 + i\varepsilon_2$)
ε_0	permittivity of vacuum
κ	extinction coefficient
Λ	mean free path
λ	wavelength in vacuum, m
ρ	resistivity, Ω m
Ω_p	plasma frequency in the Drude term, rad/s
Ω	angular frequency, rad/s
ω_p	plasma frequency in the Lorentz term, rad/s

Subscripts

c	calculated
f	film
j	index
m	measured
s	substrate

deposited by radio-frequency magnetron sputtering and analyzed the inhomogeneities with an effective medium theory. Davazoglou et al. [21] determined the dielectric function of a 200-nm-thick tungsten film at wavelengths from 0.19 to 0.82 μm and found large disagreement with the bulk values reported in Ref. [14,17]. Gravier et al. [22] extracted the thickness and optical conductivity of several transition metals with body-centered-cubic (bcc) crystal structures at wavelengths from 0.22 to 3.9 μm. They measured the transmittance and reflectance at oblique incidence of films with thicknesses on the order of 30 nm and explained the spectral variation in the ultraviolet and visible regions by interband transitions. Nestell et al. [23] and Nestell and Christy [24] investigated the optical properties of different types of evaporated metal films, including tungsten, with thicknesses from 20 to 200 nm in the wavelength region from 0.19 to 2.5 μm. These studies reported that the optical constants of polycrystalline thin films are akin to the corresponding bulk values with microstructural effects factored in. All of the above studies are for the stable tungsten phase (bcc α-W) and none of them extend to wavelengths longer than 4 μm.

Tungsten will in general form a polycrystalline film when it is deposited, although amorphous tungsten films have also been observed for as-deposited films [1,25]. In principle, tungsten can be annealed to crystallize into a single crystal, but the annealing temperature would have to reach about 2400 °C [2,3], which is much higher than the melting point of most substrates. Alternatively, single crystal tungsten can be fabricated at lower temperatures, but the film would need to be extensively worked via rolling, drawing, or mechanical deformation [1]. This is impractical for thin-film applications. Since tungsten films have been considered as an interconnect material in microelectronics, the structural and electrical properties have been extensively studied [26–28]. The density, resistivity, and other properties of the film vary greatly with deposition methods and conditions [25–32].

Tungsten films may exhibit three distinct crystal phases [1,33–36]. The most stable one is the α-W bcc phase, with the highest density and lowest resistivity, as in most studied bulk tungsten and tungsten films. There also exist two metastable phases that can occur at low deposition temperatures and with small film thicknesses. The β-W phase is an A-15 type bcc crystal (W_3W), which was initially thought to be a W_3O compound due to the similar X-ray diffraction patterns [33,34]. The γ-W phase, which can only exists in thin films, has a face-centered-cubic (fcc) structure and the lowest density [1,34–36]. The resistivity values for β-W are generally more than an order of magnitude higher than that of the bulk tungsten [26,27]. These metastable crystal phases will transform irreversibly to α-W at elevated temperatures [1,30,31,36].

At present, the infrared optical properties of thin-film tungsten are not well understood, particularly for the metastable phases. In the present study, four films were deposited on silicon substrates using DC magnetron sputtering with or without annealing. X-ray diffraction, Rutherford backscattering, X-ray photoelectron spectroscopy, scanning electron microscopy, and atomic force microscopy were used to characterize the sample phases and morphology. The transmittance and reflectance of the samples were measured from 1 to 20 μm wavelengths. The dielectric function of each sample was obtained by fitting the measured radiative properties using the Drude–Lorentz dispersion with adjustable parameters. The Hall effect and sheet resistance of one of the samples were also measured to compare the transport properties with the optical parameters in the Drude model.

2. Sample fabrication and characterization

Four samples were deposited with DC magnetron sputtering under the same conditions but with different combinations of pre- and post-deposition treatments. The samples were deposited in an Ar gas flow rate of 25 sccm and a power of 50 W. The substrates were maintained at a constant temperature of 350 °C with a tungsten filament lamp, and monitored with a calibrated radiation thermometer throughout the deposition process. The deposition time was 4 min to achieve a nominal film thickness of 70 nm. The substrates were square (1 1 0) silicon wafers with a diagonal of 20 mm. The wafers were 770 μm thick measured with a micrometer, double side polished, with a resistivity of approximately 100 Ω cm. Prior to deposition, two of the silicon wafers were ion-cleaned to remove any native oxide layer. This was done to investigate the possibility of diffusion of tungsten into the silicon layer. While there was no evidence of interfacial diffusion, an effect on the growth of the tungsten film was observed and will be discussed in more detail. Two of the samples were annealed for 1 h at 800 °C in vacuum at 1.3×10^{-6} Pa (10^{-8} Torr) to prevent any unintentional oxidation. The results show a drastic change in properties between annealed and unannealed samples. Table 1. shows the treatments performed on each sample, as well as the