Fabrication and characterization of aluminum, gold-tin and titanium-tungsten alloys for mid-infrared plasmonic applications

J Spettel\textsuperscript{1,2,4,*}, G Stocker\textsuperscript{1,4}, T D Dao\textsuperscript{2}, R Jannesari\textsuperscript{3}, A Tortschanoff\textsuperscript{2}, P Saeidi\textsuperscript{3}, G Pühringer\textsuperscript{3}, F Dubois\textsuperscript{2}, C Fleury\textsuperscript{3}, C Consani\textsuperscript{2}, T Grille\textsuperscript{1}, E Aschauer\textsuperscript{1}, M Moridi\textsuperscript{2} and B Jakoby\textsuperscript{3}

\textsuperscript{1} Infineon Technologies Austria AG, 9500 Villach, Austria
\textsuperscript{2} Silicon Austria Labs GmbH, 9524 Villach, Austria
\textsuperscript{3} Institute for Microelectronics and Microsensors, Johannes Kepler University Linz, 4040 Linz, Austria
\textsuperscript{4} These authors contributed equally to this work.
*corresponding author, E-mail: Jasmin.Spettel@silicon-austria.com

Abstract. We numerically and experimentally investigate aluminum metal (Al), gold-tin (AuSn) and titanium-tungsten (TiW) metallic alloys as plasmonic materials in the mid-infrared (MIR) region using spectroscopic ellipsometry and reflection measurements of gratings. The angle dependence of the specular reflectance of shallow gratings is investigated using a free-beam measurement setup and compared to simulations. It is shown that the deep and narrow resonances observed for all three materials match the associated prediction from simulations.

1. Introduction

Due to the great potential applications of plasmonics and photonics in the mid-infrared (MIR) spectral range, the research interest within these fields have increased rapidly in recent years. Potential applications are for example waveguides [1], photonic integrated circuits [2], selective thermal emitters [3] or IR detectors [4]. Even though many groups already searched for alternative plasmonic materials, such as silicides, transparent conducting oxides, doped semiconductors, carbides and many more, most plasmonic applications are still based on gold (Au) and silver (Ag) [5,6]. Within this work, we present aluminum (Al), gold-tin (AuSn) and titanium-tungsten (TiW) as alternative plasmonic materials in the MIR regime. Al is very cheap and a thin native oxide layer serves as protection from chemical reactions with the environment [7]. AuSn is a very soft material with a low melting point [8] and thus can be used for molding nanoimprint lithography or 3D printing. TiW on the other hand is resistant to high temperatures [9] and hence is suitable for thermal devices, such as thermal emitters [10]. In addition, it is a common material for electrodes in electronics, leading to the advantage of prospective standard fabrication.

In this study, we first show spectroscopic ellipsometry measurements of the proposed materials. Then, the materials are tested regarding their usability for surface plasmon polariton (SPP) excitation using a grating configuration. The experimental data are also compared to simulations and show good agreement. All three materials exhibit strong and narrow resonances [11].
2. Experimental
First, a spectroscopic ellipsometry study of the proposed plasmonic materials was performed. Therefore, a sample with a 100 nm thick sputtered layer for each material was prepared. Details of the fabrication process are given in [11]. The ellipsometry measurement was performed at Semilab (SE-2000 combined with IRSE extension for full UV-MIR spectroscopic ellipsometry) and the retrieved data were modeled with a Drude-Lorentz model. In Figure 1a) and b) the real and imaginary part of the retrieved relative permittivity of Al, AuSn and TiW are compared to literature values of gold (Au) and silver (Ag) [12]. Within the investigated spectral range (wavelength of 0.25 µm – 20 µm) all three materials show a negative real part of permittivity, indicating them as promising candidates for plasmonics. The values of Al are even comparable with those of Au and Ag. The imaginary part of the relative permittivity is an indicator for the losses of the material. Similarly, Al is comparable with Au and Ag, whereas AuSn and TiW are expected to have lower losses.

Figure 1: Comparison of a) real part and b) imaginary part of complex permittivity of the experimental data of Al, AuSn and TiW retrieved by spectroscopic ellipsometry with literature values of Au and Ag, taken from [12]. This figure is taken from [11].

The proposed plasmonic grating structures were fabricated on 8-inch silicon (Si) substrates in the cleanroom facilities of Infineon Technologies Austria AG. A schematic of the layer stack is shown in Figure 2a). Further details about the fabrication process are provided in our published paper [11]. In order to observe a resonance around an incidence angle of 30°, the grating period was chosen to be 2.8 µm (1.6 µm groove width) and the wavelength close to 4.2 µm (limited by the tunability of the laser). For characterization, a free-beam reflection measurement was carried out. Figure 2b) shows a schematic of the measurement setup, which is described in [11].

Figure 2: a) Layer stack of the gratings (adapted from [11]). b) Free beam measurement setup. The double-arrows indicate the p-polarization of the laser light. c) Top view SEM image of a polycrystalline Si grating with 100 nm Al coating. The grooves are indicated by the double-arrow. d) AFM measurement of one period of an Al coated grating with 225 nm depth.

Furthermore, the surface roughness of the gratings was investigated using a scanning electron microscope (SEM, Thermo Scientific Helios G4) and an atomic force microscope (AFM, Veeco Dimension 3100, Digital Instruments). Figure 2c) depicts an SEM image in top view showing the surface morphology of a polycrystalline Si grating coated with 100 nm Al. The large grains in the grooves (grooves are indicated by the double-arrow in the figure) have their origin in the structure of the polycrystalline Si layer after the etching process [11]. Figure 2d) depicts an AFM measurement of one period of an Al coated grating. Accordingly, the roughness is about 53 nm within the grooves (area 2) and 35 nm elsewhere (area 1).
In addition to the free-beam reflection measurement, the reflectance spectra of the gratings were simulated using a rigorous coupled-wave analysis software (RCWA) (DiffractMOD, Synopsys’ RSoft package). Thereby, orders -3 through +3 were considered.

3. Results and discussion

Figure 3a), b) and c) depict the angle dependence of the specular reflectance at gratings with a depth of 150 nm and a coating of 100 nm sputtered Al, AuSn and TiW, respectively. Each left panel shows the measurement result, whereas the right panels depict the specular reflectance retrieved from simulations. In addition, the CO$_2$ absorption band is indicated by the shaded rectangle in the left panel in Figure 3a). As expected from the grating equation $k_{SPP} = k_0 \sin(\theta) \pm mG_x$ [13] the resonance dip moves to longer wavelengths for larger angles of incidence $\theta$. Here $k_{SPP}$ and $k_0$ are the wavenumber of the SPP and the incident wave, respectively, $m$ is an integer and $G_x = \frac{2\pi}{P}$ is the wavenumber of the grating with period $P$. Furthermore, the resonance dip is asymmetric (Fano-like) due to the coupling between the surface wave, which is a bound state, and the diffraction from the periodic grating, which is a leaky wave [14]. Thus, the specular reflection towards shorter wavelengths regarding the resonance dip is attenuated in comparison to the specular reflectance towards longer wavelengths. In order to determine the width of the resonance (full width at half maximum – FWHM) the data at an incidence angle of 26° were fitted using a Fano-formula [15]:

$$R \propto \frac{(F \gamma + \lambda \lambda_0)^2}{(\lambda - \lambda_0)^2 + \gamma^2} + B.$$

Here $R$ is the reflectance, $F$ is the Fano-parameter, $\gamma$ the resonance width, $\lambda$ the wavelength, $\lambda_0$ the center wavelength of the resonance dip and $B$ the offset. For Al a width of 4.7 nm, for AuSn 9.7 nm and for TiW 11.6 nm was determined (the simulations yielded widths of 5.5 nm, 11.5 nm and 16.9 nm, respectively). The fitted curve together with the measurement data is shown in the inlets of Figure 3. The broadening of the resonance from Al to AuSn to TiW is consistent with the retrieved relative permittivities, shown in Figure 1. Overall a good agreement between the measurements and the simulations was obtained. Small deviations are explained by the uncertainty of the zero-angle ($\pm1^\circ$), leading to a slight shift in the position of the resonance, not perfectly p-polarized light during the measurements as well as by small variations in the fabrication process leading to slight deviations of the grating dimensions (period, groove width, side wall steepness). In addition, the surface roughness is not included in the simulations. See [11] for more details and the results of the gratings with 225 nm and 375 nm depth.

4. Conclusions

We have investigated Al, AuSn and TiW both numerically and experimentally as alternatives to Ag and Au for plasmonic applications in the MIR spectral range. A spectroscopic ellipsometry measurement
was performed to retrieve the optical properties of the proposed materials. The materials show good plasmonic properties in the MIR region. As a demonstration, we fabricated a set of plasmonic gratings using Al, AuSn and TiW. Strong SPP resonances were observed from the fabricated gratings at about 4.2 µm resonance. FWHMs were obtained with 4.7 nm for Al, 9.7 nm for AuSn and 11.6 nm for TiW. A good agreement between experimental data and simulations was observed.

Acknowledgements
This work was performed within the PICASSO-project funded by the Bundesministerium für Klimaschutz, Umwelt, Energie, Mobilität, Innovation und Technologie in the framework of the program "Produktion der Zukunft" (Prj. Nr. 871417) and partly supported by the COMET K2-Center Symbiotic Mechatronics. Furthermore, the authors want to thank the involved staff working at the cleanroom of Infineon Technologies Austria AG, Villach, for their kind support with the fabrication of the structures, T. Ostermann for the mask layouts and L. Makai and A. Ertl at Semilab for their kind support in spectroscopic ellipsometry measurement.

References
[1] Tetienne J-P et al. 2010 Injection of midinfrared surface plasmon polaritons with an integrated device Appl. Phys. Lett. 97 211110
[2] Ono M, Taniyama H, Xu H, Tsumekawa M, Kuramochi E, Nozaki K and Notomi M 2016 Deep-subwavelength plasmonic mode converter with large size reduction for Si-wire waveguide Optica 3 999
[3] Miyazaki H T, Ikeda K, Kasaya T, Yamamoto K, Inoue Y, Fujimura K, Kanakugi T, Okada M, Hatade K and Kitagawa S 2008 Thermal emission of two-color polarized infrared waves from integrated plasmon cavities Appl. Phys. Lett. 92 141114
[4] Chang C-C, Sharma Y D, Kim Y-S, Bur J A, Shenoi R V, Krishna S, Huang D and Lin S-Y 2010 A Surface Plasmon Enhanced Infrared Photodetector Based on InAs Quantum Dots Nano Lett. 10 1704–9
[5] West P R, Ishii S, Naik G V, Emani N K, Shalaev V M and Boltasseva A 2010 Searching for better plasmonic materials Laser Photonics Rev. 4 795–808
[6] Zhong Y, Malagari S D, Hamilton T and Wasserman D 2015 Review of mid-infrared plasmonic materials J. Nanophotonics 9 093791
[7] Gerard D and Gray S K 2014 Aluminium plasmonics J. Phys. Appl. Phys.
[8] Lee C H, Wong Y M, Doherty C, Tai K L, Lane E, Bacon D D, Baiocchi F and Katz A 1992 Study of Ni as a barrier metal in AuSn soldering application for laser chip/submount assembly J. Appl. Phys. 72 3808–15
[9] Marx D R, Turn J C and Shi J 1999 Tungsten titanium targets for VLSI device fabrication (Materials Research Corporation)
[10] Laroche M, Arnold C, Marquier F, Carminati R, Greffet J-J, Collin S, Bardou N and Pelouard J-L 2005 Highly directional radiation generated by a tungsten thermal source Opt. Lett. 30 2623
[11] Spettel J et al. 2021 Aluminium, gold-tin and titanium-tungsten alloys for mid-infrared plasmonic gratings Opt. Mater. Express 11 1058
[12] Rakić A D, Djurišić A B, Elazar J M and Majewski M L 1998 Optical properties of metallic films for vertical-cavity optoelectronic devices Appl. Opt. 37
[13] Sambles J R, Bradbery G W and Yang F 1991 Optical Excitation of Surface Plasmons: an introduction Contemp. Phys. 32 173–83
[14] Miroshnichenko A E, Flach S and Kivshar Y S 2010 Fano resonances in nanoscale structures Rev. Mod. Phys. 82 2257–98
[15] Luk’yanchuk B, Zheludev N I, Maier S A, Halas N J, Nordlander P, Giessen H and Chong C T 2010 The Fano resonance in plasmonic nanostructures and metamaterials Nat. Mater. 9 707–15