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Compositional dependence of the optical conductivity of $Ni_{1-x}Pt_x$ alloys ($0 < x < 0.25$) determined by spectroscopic ellipsometry

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ABSTRACT

We measured the ellipsometric angles as a function of photon energy from 0.76 to 6.6 eV of 10 nm thick $Ni_{1-x}Pt_x$ alloy ($0 < x < 0.25$) films deposited on thick thermal oxides. Using basis spline functions and Drude–Lorentz oscillator fitting, we determined the dielectric functions and optical conductivities of our alloy films. We describe techniques to increase the accuracy of our measurements and data analysis. We find absorption peaks near 1.6 and 4.8 eV due to interband optical transitions. There is a significant broadening of these peaks with increasing Pt content. Annealing the metals at 500 °C for 30 s increases the optical conductivity.

1. Introduction

The complex dielectric functions of metals are less well known than those of insulators and semiconductors [1], because it is hard to achieve comparable purity and crystallinity in metals. Metals can be deposited on various substrates (especially glass or SiO_2 on Si) as poly-crystalline films by evaporation, sputtering, electro-plating, or chemical vapor deposition. Single-crystalline metals are rare. Therefore, the optical response of metal films will depend on the deposition technique and parameters such as grain size, texture, film thickness, and impurity content [2]. Many metals (especially alkali metals and rare earths) are highly reactive. Therefore, the optical constants of noble and near-noble metals such as Au, Ag, and Pt are known with the highest accuracy.

Our present work describes measurements to determine the optical constants of Ni and $Ni_{1-x}Pt_x$ alloys as a function of composition ($0 < x < 0.25$), where x is measured in atomic percent. To be consistent, most of our alloys were deposited as thin films (10 nm thickness) on thermal oxides by physical vapor deposition (sputtering). We find a broadening of the interband optical transitions in $Ni_{1-x}Pt_x$ alloys with increasing Pt content.

Our choice of film thickness and composition is motivated by the application of similar alloys as Ohmic contacts in modern complementary metal–oxide–semiconductor (CMOS) device processing. Our results enable inline optical thickness measurements of metal contact layers using spectroscopic ellipsometry, the most common film thickness measurement technique in the semiconductor industry. In the visible spectral range, metals have penetration depths comparable to our film thickness (10 nm). We will describe specific experimental strategies to determine the optical constants of such thin films with high accuracy. We carefully discuss experimental artifacts and how to identify or reduce them.

2. Sample preparation

Most of our $Ni_{1-x}Pt_x$ films were deposited on two-side polished Si wafers with 300 mm diameter. Thick transparent SiO_2 layers were first grown as thermal oxides on the Si substrates. For convenience, we chose an oxide thickness of 200 nm, since such thermal oxides can easily be grown on front-end CMOS processing equipment. The transparent oxide below the absorbing metal thin film enhances the information available through variable-angle spectroscopic ellipsometry, since the optical path length in the oxide varies with the angle of incidence [3]. We retained one bare, unprocessed Si substrate and one wafer with thick SiO_2 thermal oxide as reference materials. To avoid reflections of light below the Si band gap from the back surface of the wafer [4] (which is incoherent with the light reflected from the front surface and leads to depolarization of the reflected beam), the back surfaces of the wafers were roughened with a sandblaster using alumina abrasive [5,4,6].

$Ni_{1-x}Pt_x$ films with varying compositions ($0 < x < 0.25$, measured as an atomic percentage) were sputtered on the thermal oxide using a commercial DC magnetron sputtering tool for 300 mm Si wafers. The wafer was kept at room temperature during deposition. Typical deposition pressures are on the order of 1 mTorr. We chose a film thickness of 10 nm, which is similar to Ni films used in CMOS device processing. The composition was varied by co-sputtering simultaneously from

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two targets with compositions of $Ni_{0.9}Pt_{0.1}$ and $Ni_{0.7}Pt_{0.3}$. The deposition rate was on the order of 1 Å/s (about 100 times slower than in the work by Johnson and Christy [7], where samples were prepared by evaporation), resulting in a deposition time of about 2 min for a 100 Å thick film.

The thicknesses and compositions of the $Ni_{1-x}Pt_x$ films were measured using X-ray reflectivity (XRR), X-ray fluorescence, [8] and sheet resistance measurements. XRR [8,9] also showed that the surface layer (oxide and roughness) thickness for similar films was on the order of 15 Å. The $Ni_{1-x}Pt_x/SiO_2$ interface is very stable. Ni diffusion in SiO_2 or nickel silicate formation can be neglected at temperatures below 600 °C, which was confirmed by XRR measurements [8]. To investigate the influence of thermal processing on the optical constants of $Ni_{1-x}Pt_x$ alloys, some samples were annealed. The most common annealing conditions were heating to 500 °C for 30 s in N_2 at atmospheric pressure. The annealing ramp rate was 20 °C/s and the O_2 partial pressure was below 8 ppm.

3. Experimental methods

Spectroscopic ellipsometry [10,11,4] measures the Jones ratio

$$\rho(E,\phi) = r_p/r_s = (tan\psi)e^{i\Delta} \quad (1)$$

versus photon energy E and angle of incidence ϕ. r_p and r_s are the complex Fresnel reflectance ratios for p- and s-polarized light. ψ and Δ are known as the ellipsometric angles. Under ideal conditions, the reflected beam should be totally polarized, if the incident beam is linearly or elliptically polarized. In practice, some of the reflected intensity is unpolarized even for total polarization of the incident beam. This is known as depolarization. It can be caused by incoherent reflections from the back surface (which we eliminated by roughening the backside of our wafers), by film thickness variations (on the order of 2% across the beam spot for our samples and measurement conditions), by the focusing of the incident beam on the sample, or by the bandwidth of the monochromator (about 2 nm for our measurements) [4].

We acquired ψ and Δ and the depolarization on a vertical variable-angle-of-incidence rotating-analyzer ellipsometer with a computer-controlled Berek waveplate compensator (J.A. Woollam Co., Lincoln, NE, USA; Model V-VASE-DUV-XNIR). We varied the incidence angles between 20° and 80°. The detector and optics are suitable for measurements from 0.5 to 6.6 eV, but the choice of the optical fiber between the monochromator and the polarizer-sample-analyzer assembly limits spectra to the IR range (0.5 to 4.5 eV) or the UV range (0.76 to 6.6 eV). This instrument uses a triple-grating, double-chamber Czerny–Turner monochromator with 160 mm focal length. The monochromator has variable entrance and middle slits (0 to 2000 μm). The exit slit width is determined by the diameter of the optical fiber used to connect the monochromator with the goniometer base of the ellipsometer (usually 200 μm). In the visible and UV spectral range, the linear dispersion of the monochromator is 2.3 nm/mm with 1200 lines per mm ruled gratings. We usually chose a step size of 20 meV. These datasets required about 24 h for data acquisition on one sample.

Typical spectra are shown in Figs. 1 and 2.

Fig. 2 shows the depolarization of the reflected beam (as a percentage of total reflected intensity) versus photon energy for various monochromator entrance/middle slit widths. It can be seen that the dominant source of the depolarization in the UV is the dispersion of the monochromator. The depolarization can be reduced significantly with a monochromator entrance/middle slit width of 1 mm, which corresponds to a spectral resolution of 2.3 nm. Reducing the entrance/middle slit width further increases the noise in the spectra, as shown in Fig. 2. Given these results, all our spectra were acquired with an entrance/middle slit width of 1 mm. This reduces the depolarization peaks at 4.3 and 6 eV. The origin of the depolarization peaks at 1 and 3.5 eV is not known. These peaks were not affected by the monochromator slit width or other experimental parameters. Similar depolarization peaks are found for a thick oxide on Si (without Ni), but they disappear in thick Ni films or on a bare Si substrate and therefore are related to interference effects.

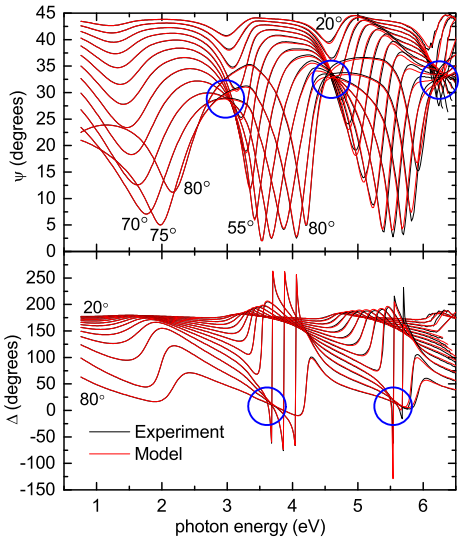

Fig. 1. (Color online) Ellipsometric angles ψ and Δ as a function of photon energy for a 10 nm thick $Ni_{1-x}Pt_x$ alloy ($x = 0.1$) on 220 nm oxide deposited on an undoped Si substrate, acquired with incidence angles ranging from 20°to 80°. Experimental data are shown in comparison with fits to the data using a Drude–Lorentz oscillator for the Ni–Pt optical constants. The circles show focal points, where ψ or Δ is independent of incidence angle (for large angles). The incidence angle ϕ is indicated for some spectra. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 1 shows the ellipsometric angles for an as-deposited 10 nm thick $Ni_{1-x}Pt_x$ alloy ($x = 0.1$) on SiO_2. ψ is always below 45°, which indicates that $|r_p| < |r_s|$ for all energies and incidence angles. (For a bare oxide film without Ni, ψ reaches peaks close to 90°.) The ψ spectrum shows minima (interference fringes) near 2 eV, 4 eV, and 5.5 eV. They originate from the thick SiO_2 layer below the metal. The fringes shift with the incidence angle due to variations in the path length. Small incidence angles (near-normal conditions) only yield shallow ψ minima, while large incidence angles (above 40°) result in steep ψ minima. Since we observe strong interference effects (with ψ almost reaching zero) over the entire spectral range, we conclude that the 10 nm thick metal film is essentially transparent over the entire spectral

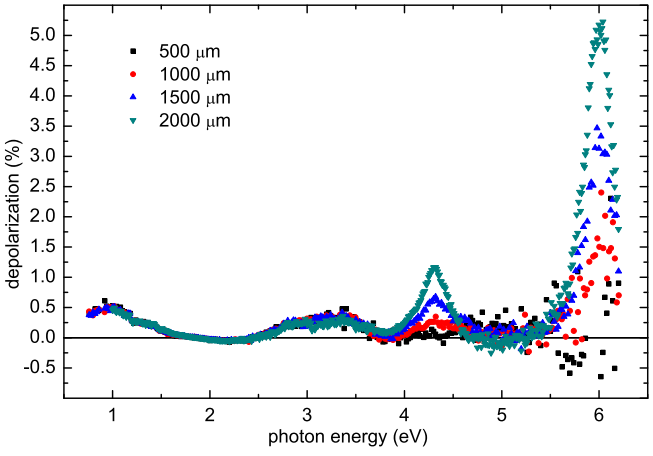

Fig. 2. (Color online) Depolarization of the reflected beam as a function of photon energy for $Ni_{0.75}Pt_{0.25}$ annealed at 500 °C (30 s) for 70° angle of incidence and different slit widths ranging from 500 to 2000 μm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)