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Silicides for infrared surface plasmon resonance biosensors

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ABSTRACT

Pt-, Pd-, Ni-, and Ti-silicide films on silicon were evaluated as conducting hosts for surface plasmon polaritons (SPP) in proposed long-wave IR (LWIR) attenuated total reflection biosensors. Original LWIR complex permittivity data was collected, from which SPP properties were determined and compared with those for noble metals. LWIR SPPs on silicide films were found to offer enhanced sensitivity to thinner biological entities than when usual metal films are used.

INTRODUCTION

Thin dielectric films on a conducting surface strongly affect the bound electromagnetic waves known as surface plasmon polaritons (SPP), providing a means for real-time label-free sensing and monitoring of biological entities from molecules to cells. Surface plasmon resonance (SPR) biosensors have become a sensitive label-free method to study biological interactions,[1-3] e.g. those marketed by Biacore or Texas Instruments. Established sensors are based on wavelength and angle dependent resonances in attenuated total reflection (ATR) devices using visible/near-infrared light.

We propose LWIR operation using silicon-based materials because of a number of potential advantages. The LWIR is defined roughly as the 8-12 micron wavelength range, which corresponds to a band of high atmospheric transmission. Large changes for the refractive index are expected near the characteristic LWIR vibrational frequencies of biomolecules, giving potentially better specificity than can be achieved at visible wavelengths. Semiconductor quantum cascade lasers have become available throughout this range. Silicon is highly transparent here, and silicon-based devices offer benefits of integrated manufacturing, miniaturization, micro-fluidic sampling. Because the ATR method works in the regime of total internal reflection, silicon allows observation of larger index values for the sample of interest, up to ~3.4, than can be observed in the visible with glass prisms (n ~1.5).

This paper considers conducting silicides as IR surface plasmon hosts as opposed to the usual noble metals. Silicides may be grown by standard processing procedures directly on the polished surfaces of Si prisms or wafers. The lower carrier concentration and plasma frequency of silicides relative to metals pushes the surface plasmon dispersion curve farther from the light line in the IR, which is advantageous for observing resonances in the ATR configuration. Surface plasmons on silicides offer tighter mode confinement to increase the sensitivity to thin

dielectric adsorbates.[4] Original LWIR permittivity data was measured for Pt-, Pd-, Ni- and Ti-silicides, for which LWIR SPP characteristics, including mode profiles, resonance line spectra, and the effect of adsorbed dielectric films are then calculated. CO_2 laser wavelengths fall squarely in the middle of the LWIR range. Since the extinction coefficient of liquid water is about half as large at the 9.25 μm wavelength tuning limit of the CO_2 laser as it is at the 10.6 μm limit, we will emphasize numerical results for 9.25 μm.

THEORY

Fig. 1 presents a schematic of a SPR biosensor, consisting of a prism, conducting film, and flow channel. In this so-called Kretschmann configuration, the prism allows matching of the photon and SPP momenta, enabling optical excitation of the SPP at the conductor-channel interface. The SPP wavevector is[5]

$$k_{spp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon(\omega)_{metal}\varepsilon_{dielectric}}{\varepsilon(\omega)_{metal}+\varepsilon_{dielectric}}} = k_{spp}{}' + ik_{spp}{}'' \tag{1}$$

where $\varepsilon(\omega)_{metal}$ is the complex, frequency-dependent permittivity of the conducting film and $\varepsilon_{dielectric}$ is the permittivity of the material above the sensor surface. The surface plasmon resonance condition is given by

$$k_{spp}{}' = n_{prism}\frac{\omega}{c}\sin(\vartheta_{res}) \tag{2}$$

where n_{prism} is the refractive index of the prism and θ_{res} the incidence angle for peak SPP excitation, which is observed as a resonant decrease in reflected light.

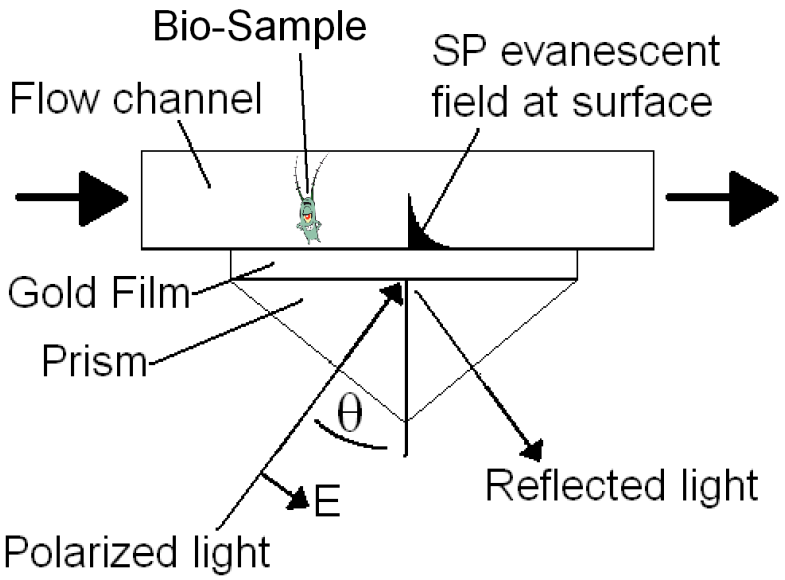

Figure 1: Schematic of SPR Biosensor, showing usual glass prism with deposited gold film for visible or near-IR operation.

Biological entities with even small differences in permittivity from that of the fluid matrix can significantly change the resonance angle. It is reasonable to suggest that the exponentially-decaying evanescent surface plasmon field, which extends into the flow channel, must have substantial overlap with the bio-sample for any change to be observed. If the field extent is much larger than the characteristic dimension of the bio-sample, the perturbation should be small. The SPP field penetration *L*, given by

$$L = \left[\frac{\omega}{c} \mathrm{Re}\left\{ \sqrt{\frac{-\varepsilon_{dielectric}^{\ 2}}{\varepsilon(\omega)_{metal} + \varepsilon_{dielectric}}} \right\} \right]^{-1}, \qquad (3)$$

increases rapidly with optical wavelength. For noble metals, *L* is much larger than the characteristic size of biomolecules at LWIR wavelengths, leading to poor sensitivity to them, and this is our motivation to consider other conductors as SPP hosts.

EXPERIMENT

Alternating layers of silicon and metal (platinum, palladium, nickel and titanium) were deposited onto clean silicon substrates by electron beam evaporation, according to expected silicide stoichiometry and reasonable estimates for interdiffusion rates. The deposited layers were then annealed at 800ºC for at least 2 hours to form the silicides. Silver and gold films were deposited on silicon for comparison. Four-point probe resistivity values were found to be comparable to accepted values[6] (see table 1). A profilometer determined film thickness, which in all cases was much larger than the skin depth at IR wavelengths. Complex permittivities[7] were determined using J.A. Woollam IR-VASE and V-VASE ellipsometers in the IR and visible wavelength regions, respectively.

Silicide	Nominal ρ (μΩ-cm)	Measured ρ (μΩ-cm)	Measured Thickness (nm)
Ni	~ 50	31	230
Pd	30 - 35	21	160
Pt	28 - 35	31	200
Ti	14 - 18	12	180

Table 1: Nominal resistivities,[6] measured resistivities, and measured thicknesses of metal silicide films.

RESULTS

Real and imaginary parts of the permittivity are compared in Fig. 2 for palladium silicide and silver. (Visible range values for silver are from Ref. [8].) The IR values for gold and silver are very similar but significantly different than those for silicides, which are very similar to each other. Hence, only one of each group (silver and palladium silicide) is presented in Fig. 2 for clarity. At 9.25 μm wavelength (0.134 eV photon energy), ε_{Ag} = -5397+ i 1463, and ε_{Pd2Si} = -527 + i 260.

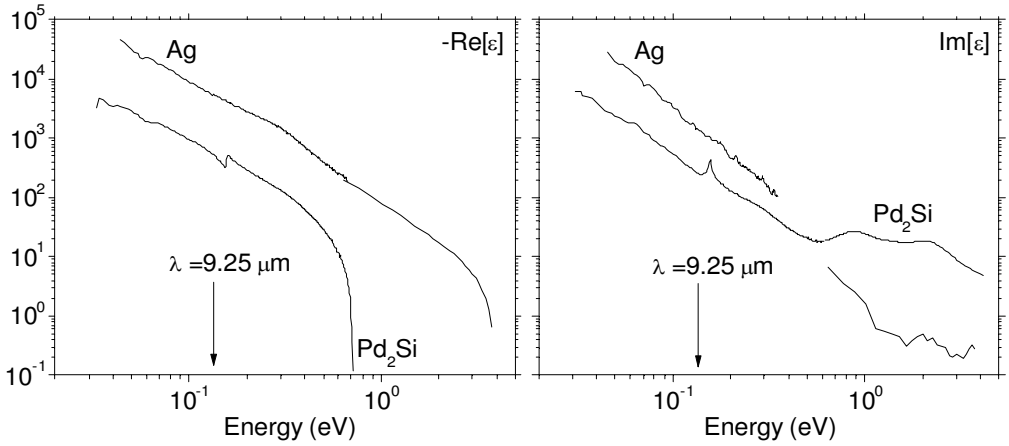

Figure 2: (left) Negative real part of permittivity for palladium silicide and Ag. (right) Imaginary parts. The energy corresponding to 9.25 μm wavelength is indicated in each figure.

Field penetration depths *L* are calculated from Eq. 3, assuming a real index for water of 1.333, and plotted in Fig. 3. At 9.25 μm wavelength, *L* ~ 60 μm for Ag and ~ 20 μm for Pd_2Si. In other words, the mode confinement is 3x tighter for the silicide.

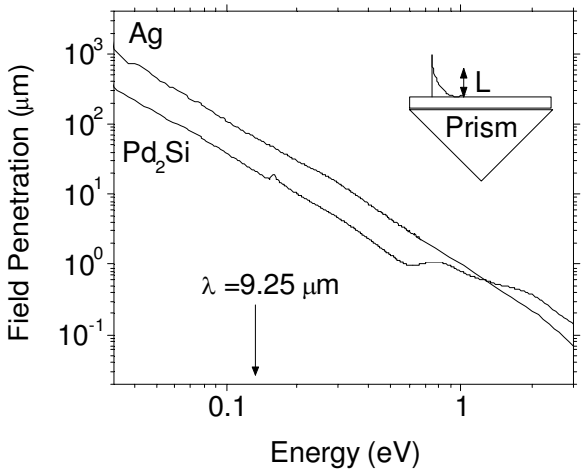

Figure 3: Field penetration into flow channel. Inset: Schematic of prism, conducting film, evanescent SPP fields, and characteristic penetration depth *L*.

Reflectance calculations for layered media[9] based on Fresnel's equations give the SPP resonance spectra presented in Fig. 4 at 9.25 μm wavelength. The incident medium is silicon (n=3.42). The Ag thickness was taken as 10 nm and the Pd_2Si thickness 45 nm to give the same optical thickness and the deepest resonances. The indices of the flow medium (water) and of the bio-sample were taken to have values 1.333 and 1.35, respectively, and the spectrum is calculated for different bio-sample thicknesses. For a hypothetical bio-sample much thicker than *L*, the shift in the resonances are comparable for the two conductors, but the thickness regime over which the resonance shifts most rapidly differs due to the 3-fold difference in the SPP *L*-value for each.

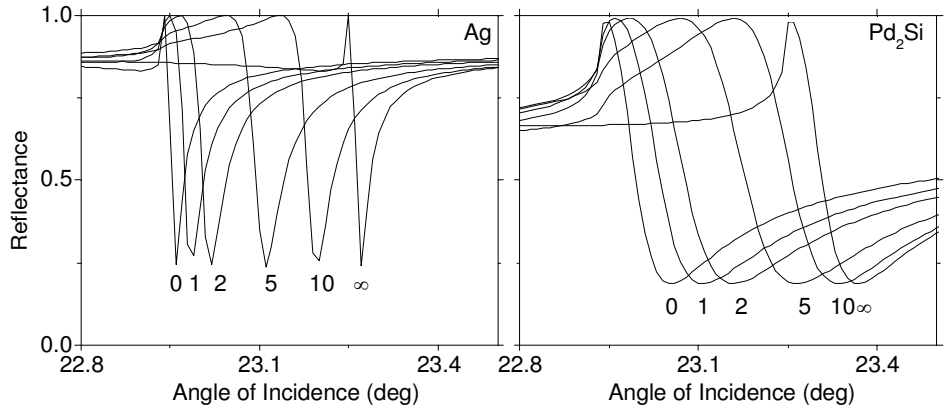

Figure 4: Surface plasmon resonances for silver (left) and Pd_2Si (right) at 9.25 μm. The biolayer thicknesses in micrometers is indicated for each curve.

To more effectively compare the thickness regimes of rapid resonance shift, the shift is plotted as a function of bio-sample thickness in Fig. 5. Shaded boxes indicate the thickness ranges for 10-90% of the full possible shift, showing that the silicide-based sensor is sensitive to bio-samples roughly 3 times thinner than is the silver-based sensor. This range is approximately 600 nm to 10 microns, i.e. suitable for detection of bacteria and cells, but not for viruses or biomolecules.

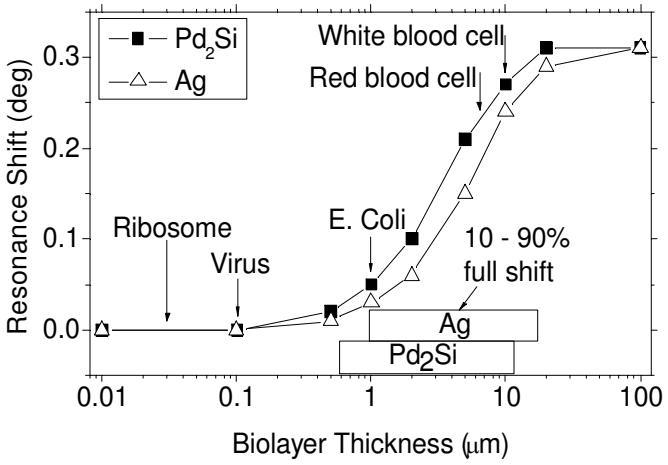

Figure 5: Resonance shift for silver and palladium silicide as the biolayer thickness is increased 9.25 μm wavelength.

SUMMARY AND DISCUSSION

Original IR permittivity data and calculation of SPP properties show that silicides offer ~3x tighter LWIR mode confinement than do noble metals. Thus, in principle, the silicides are better suited in an SPR sensor for thinner bio-samples. On the other hand, the LWIR mode penetration into the flow channel is still so large that the region of sensitivity is limited to rather large biological entities such as bacteria and cells. To achieve sensitivity to biomolecules, which have sub-100 nm dimensions, it will necessary to consider conductors with even lower conductivity and lower plasma frequencies. Our previous work [4] suggests that heavily-doped silicon is a possibility, and this retains the advantages of using silicon prisms already enumerated

in the introduction. We note that the resonance line widths for the silicides are much broader than for noble metals. This means that within the thickness regime of highest sensitivity, the silicides will be less sensitive to small thickness (or permittivity) differences. This is an additional reason to continue the search for and study of alternative low plasma frequency materials for SPR biosensors.

The calculations presented here used water as a carrier for biomolecules in the flow channel and n = 1.333 with no imaginary part. In fact, at 9.2 μm wavelength the index[10] is 1.257 and extinction coefficient is 0.0518. Correcting for this difference produces small but noticeable changes in the calculated resonance spectra, but the main conclusions are unaffected. For the LWIR, the lowest absorption by liquid water falls between 7.8 and 8.4 μm wavelength, which is compatible with a quantum cascade lasers.

ACKNOWLEDGMENTS

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