Optical hydrogen detection with periodic subwavelength palladium hole arrays

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The extraordinary transmission of infrared light through subwavelength rectangular hole arrays of palladium is used to detect hydrogen. The main resonance peak of rectangular hole arrays is found to shift upon exposure to hydrogen. Experimental evidence of the change in the Pd phase, producing a shift toward longer wavelengths of the main resonance peak, is presented and supported by simulations that agree with experimental observation. The all-optical and selective detection scheme of hydrogen produces large peak shifts that enable the detection of hydrogen concentration near the lower flammability threshold in air. © *2009 American Institute of Physics*. [doi:10.1063/1.3224890]

Due to safety concerns and the poor public perception about hydrogen (H_2), the development of highly reliable H_2 detection techniques is of utmost importance in advancing the hydrogen-based economy. In this respect, all-optical detection schemes have attracted much attention owing to their safety record. However, the current approaches still lack selectivity and sensitivity. Thus, new detection schemes need to be investigated. In this letter, a detection scheme based on the extraordinary transmission effect[1,2] is proposed. In the extraordinary transmission effect, the coupling of light with surface plasmon polaritons on the surface of a periodic hole array allows for light to be transmitted through subwavelength holes at characteristic wavelengths. The wavelengths of these resonant transmission peaks correspond to a match between the surface plasmons momentum and the incident photon momentum. The proposed detection scheme differs from the widely adopted approach using surface plasmons to detect biological or chemical substances in which the optical properties of the metal-air interface are modified by adsorption of biological/chemical substances on the metal surface.[3,4] Here, it is the metallic hole array itself that is modified through H_2 exposure by forming a Pd hydride phase, which is known for its lattice expansion[5–7] and its optical property variations.[8,9] The detection is performed by monitoring change in the resonance peak at the substrate/Pd interface of the hole array, thus making the scheme exclusively selective to H_2.

Our previous investigations into infrared transmission of periodic subwavelength Pd hole arrays have revealed a transmittance attenuation upon H_2 exposure of the main resonance peak that was predominantly caused by the lateral expansion of the Pd layer in the case of square holes.[10,11] The observed transmittance attenuation was sufficient to detect H_2 at concentrations near the lower flammability concentration of 4% in air. However, detection schemes based on transmittance attenuation are known to be sensitive to changes in the light source intensity and stray light. Thus, a more robust detection scheme needs to be developed.

In this letter, a H_2 detection scheme based on the wavelength shift of the main resonance mode of a subwavelength metallic rectangular hole array exhibiting the extraordinary transmission effect is proposed and demonstrated. The wavelength shift is produced by the formation of Pd hydride upon exposure to H_2, leading to a variation in permittivity of the Pd hole array and an increase in the aspect ratio of the rectangular holes caused by Pd lattice expansion. Simulation results show that the variations of both the permittivity and the hole shape produced shifts toward longer wavelengths, thus boosting the magnitude of the observed wavelength shifts.

The subwavelength Pd hole arrays were fabricated by direct-write electron beam lithography on Si substrates, according to the fabrication sequence illustrated in Fig. 1(a). The desired periodic feature was obtained by direct electron beam writing (F5112, Advantest, Tokyo, Japan) of a 400 nm spin-coated resist film (ZEP-520A, Zenon Corporation, Tokyo, Japan) and subsequent resist development (ZEP-N50, Zenon Corporation). A 100-nm-thick Pd thin film was deposited by sputtering on the patterned resist, and, finally, the resist was removed by a lift-off process in N,N-dimethyl acetoamide, resulting in a periodic metallic hole array. The

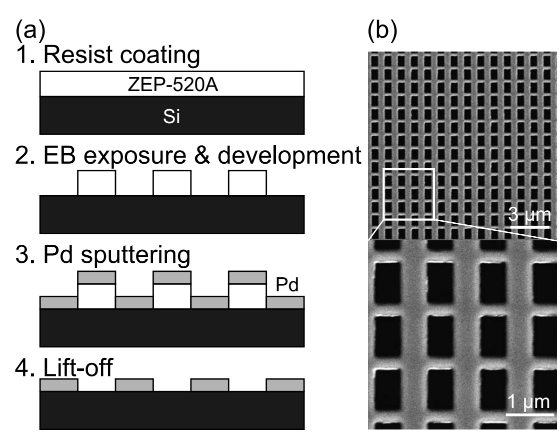

FIG. 1. (a) Fabrication sequence of the Pd hole arrays and (b) field emission scanning electron microscopy images of the fabricated hole array having a period of 1.1 μm and an aspect ratio of 1.6.

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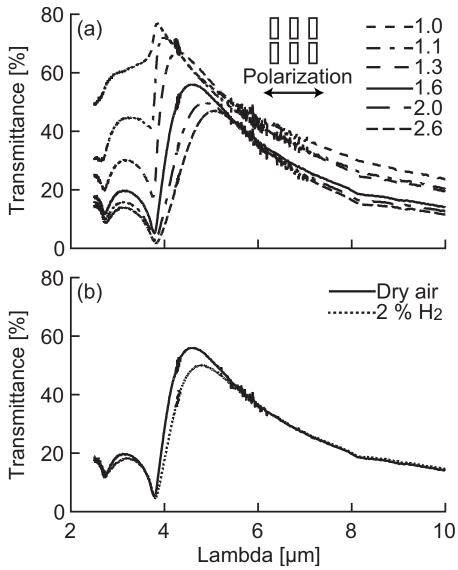

FIG. 2. (a) Measured transmittance spectra as a function of aspect ratio. (b) Observed variations in the transmittance spectrum of the hole array with an aspect ratio of 1.6 for a 2% H_2 exposure. All spectra were recorded with radiation polarized along the axis parallel to the width of the rectangles.

fabricated hole arrays had rectangular holes with a 1.1 μm lattice period. Six hole arrays were prepared with the hole dimensions (length in μm, width in μm) of (0.80, 0.80), (0.80, 0.70), (0.80, 0.60), (0.80, 0.50), (0.80, 0.40), and (0.80, 0.30), corresponding to the aspect ratio series of 1.0, 1.1, 1.3, 1.6, 2.0, and 2.6. The hole dimensions were estimated from field emission scanning electron microscope (FE-SEM, JSM-7000F, JOEL, Tokyo, Japan) images, an example of which is given in Fig. 1(b).

The zero-order transmission spectra were recorded at normal incidence through the hole arrays in the infrared region (2.5–10 μm) with a resolution of 2 nm, using a Fourier transform infrared spectrometer (Infinity FT-IR, Mattson Technology, Fremont, CA, USA), in which a gas loading cell was introduced.[10] The observed transmitted spectra of the Pd hole arrays with different aspect ratios in dry air are shown in Fig. 2(a). The shift of the main resonance peak (between 4 and 5 μm, corresponding to the (1,0) propagation mode of the array) toward longer wavelengths with increasing aspect ratio is in agreement with the observations in Refs. 12 and 13. The effect of H_2 exposure on the transmission spectrum of the array that has an aspect ratio of 1.6 is shown in Fig. 2(b), revealing a 200 nm shift of the main resonance peak toward longer wavelengths caused by H_2 exposure.

The rigorous coupled-wave analysis (RCWA) method was applied to simulate the electromagnetic wave propagation through the subwavelength Pd hole arrays.[14] We used DiffractMOD (RSoft Design Group, Ossining, NY, USA), an implementation of the RCWA method, to compute the zero-order transmission spectra, in which the frequency dependence of the relative permittivities of Pd and Si were represented by Drude's functions. The calculated and the measured positions of the (1,0) resonance mode for different aspect ratios are shown in Fig. 3(a). The positions of the simulated peaks are in good agreement with the observed positions. Therefore, a correct representation of the effect of the hole shape is achieved by the RCWA simulation. Next, the RCWA simulation is used to simulate the effects of H_2 exposure on the Pd hole arrays in the following way. Hydrogen absorption by Pd forms a Pd hydride phase, which causes an absolute decrease in the real and imaginary parts of the Pd permittivity[8,9] and a volume expansion of the original Pd lattice.[5–7] The variation in the optical properties of the Pd layer is simulated by a decrease in the absolute permittivity of Pd taken as 20%.[9] The change in the dimensions of the hole array is simulated by a 3.5% expansion of the Pd lattice, which represents full expansion at the alpha-to-beta transition near 2% H_2. The peak shift of the main resonance peak when exposed to 2% H_2 for the fabricated series of Pd hole arrays, together with the simulated shifts exposure and the simulated peak shift values are presented in Fig. 3(b). The good agreement between the observed and simulated peak shifts over the investigated range of aspect ratios is evidence for the correct representation of the effect of H_2 absorption on the Pd hole arrays. It is worth noting that not only is the saturation of the peak shift for aspect ratios larger than 1.6 correctly reproduced, but also the absolute values of the shifts are in good agreement with experimental values. The different contributions to the peak shift are simulated independently to clarify their contribution to the total shift [see Fig. 3(c)]. The decrease in the absolute value of the relative permittivity induces an increase in the resonance wavelength, which has a large contribution on the total shift. Pd expansion results in lateral expansion, which translates into a decrease in the hole size and vertical expansion, which increases the thickness. Lateral and vertical expansions have

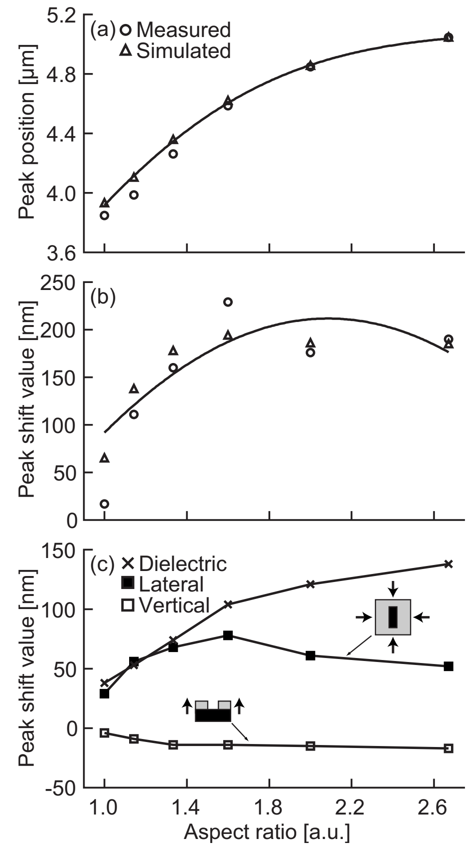

FIG. 3. (a) Comparison between the measured and simulated peak positions of the resonance Pd/Si (1,0) mode as a function of the aspect ratio of the rectangular holes. (b) Comparison between observed and simulated shifts of the (1,0) peak as a function of the aspect ratio for a 2% H_2 exposure. (c) Contributions to the resonance peak shift of the relative permittivity variation (20% decrease in absolute value of the real/imaginary parts) and of the lateral and vertical expansion (3.5%) of the Pd layer for a 2% H_2 exposure.

opposite effects on the peak shift. Lateral expansion increases the aspect ratio of the rectangular holes and therefore translates into a peak shift toward longer wavelengths, whereas vertical expansion, by increasing the Pd layer thickness, is thought to have a minor effect on the peak position for the layer thickness considered in this work (100 nm). The optimum aspect ratio for the largest wavelength shift obtained at a constant rectangle length was found to be 1.6.

In summary, a H_2 detection scheme based on the shift of the resonance peak of Pd arrays of subwavelength rectangular holes was validated by both experimental and numerical investigations. On the basis of RCWA simulation, the peak shift was attributed to the combined effects of the variation of the Pd permittivity and the hole shape, which add up to generate large wavelength shifts. The magnitude of the peak shift was found to have an optimum aspect ratio, for which a peak shift as large as 200 nm was observed at 2% H_2. As the present all-optical H_2 detection scheme is fully selective to H_2, it is expected to find applications where gas selectivity is an issue.

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