Phase jumps and interferometric surface plasmon resonance imaging

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Conditions at which phase of light demonstrates a markedly different behavior for close values of system parameters as well as the Heaviside jump are discussed and explained in terms of phase topology. On this basis, a method of interferometric surface plasmon resonance imaging is proposed and applied to develop ultrasensitive affinity array sensors with a monoatomic thickness resolution.
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Phase of a system is known to have nontrivial topological nature, since it is defined up to the value of 2π and is not defined for the zero value of system parameters. This leads to different interesting features of phase behavior, which include, e.g., topological properties of the phase of a wave function in Aharonov–Bohm experiments,[1] the Berry phase of a quantum system,[2,3] and the Pancharatnam phase of a light polarization.[4] This is also a topological property that the phase of an optical system manifests the Heaviside step-like jump and markedly different behavior for close values of system parameters when the light intensity is crossing zero.

Indeed, let us consider the phase of the light reflected from an optical system in the complex polarization plane E, where phase corresponds to the polar angle. Being plotted as a function of the incidence angle (or the light wavelength), the reflected electric field E_r forms a family of curves as shown in Fig. 1. When the set of curves E_r crosses the origin of the coordinates, the angle (wavelength) dependence of the phase of the reflected light undergoes a dramatic change. Between curve 1 with a monotonous decrease of the phase and curve 3 with a nonmonotonous increase of the phase there lies curve 2 with the π jump of the phase. It is necessary to note that the phases of neighbor points A_1 and A_3, B_1 and B_3 of curves 1 and 3, respectively, are close to each other. It is topology that totally changes the phase behavior: the position of the origin of the coordinates is different with respect to curves 1 and 3. In addition, the phase variations become much quicker as the curve is getting closer to the origin of the coordinates.

In general, if a system amplitude parameter crosses zero, then, the system total phase shows the Heaviside π jump as well as markedly different behavior for infinitesimally close values of external parameters. For example, the phase of the *p*-polarized light reflected from an optical interface near the Brewster angle shows the π jump;[5] the phase of the light reflected from the Fabry–Perot interferometer demonstrates the π jump when the reflected light amplitude crosses zero;[5] and the phase of light near the focus of a lens has π jumps along the lens axis at the points where the light intensity is zero.[5]

In particular, these considerations are directly applied to surface plasmon resonance (SPR), which represents a very important case for sensor applications. SPR is a resonant dip in an angular (wavelength) dependence of the intensity of the *p*-polarized light reflected from a metal in, e.g., the prism[6] or grating[7] configuration. The dip is usually attributed to light wave conversion to surface electromagnetic waves coupled with collective oscillations of free electrons in the metal (plasmons). Indeed, the fast change of phase of the reflected light under SPR was observed in ellipsometry measurements,[8] while the possibility of the step-like phase jumps was confirmed by direct phase visualizations using interferometry methods[9,10] and by a numerical simulation of Fresnel's formulas.[11] A remarkable SPR property consists in a dramatic dependence of the reflected light on the refractive index of a medium, which is in contact with the SPR-supporting metal. This property has been used for the development of a new generation of sensors,[12] which makes possible studies of bio and chemical interactions in thin binding films deposited on the metal.[13] In our previous works[14,15] phase-sensitive SPR interferometry sensor schemes were introduced, which showed a dramatic gain in sensor characteristics (the sensitivity to a refractive index change was estimated as 4×10^{-8} in a model experiment with different gases).[15]

Since infinitesimally small changes of system parameters can result in totally different phase behavior, one may anticipate here a large potential for an improvement of the performance of SPR-based imaging and sensor methods. Later we show that the SPR phase jump and the strong dependence of

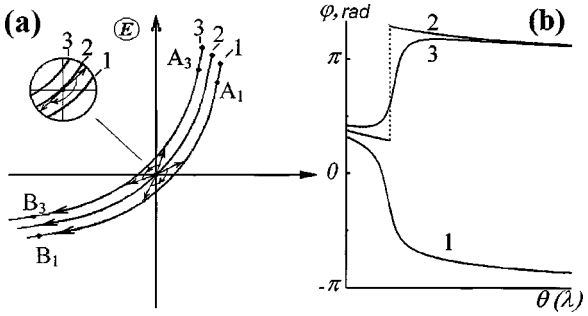

FIG. 1. (a) The set of curves of the electric field reflected from an optical system as a function of the incidence angle θ (or the light wavelength λ) plotted for different system parameters in complex plane. (b) The corresponding phase φ, as a function of θ (or λ).

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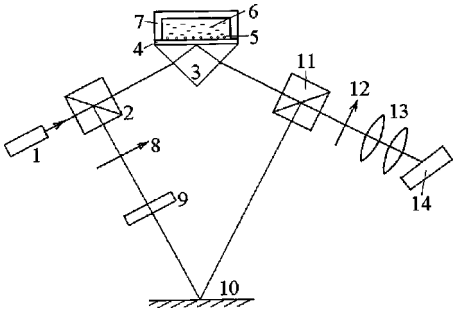

FIG. 2. Schematic of the optical setup for the interferometric SPR imaging: (1) HeNe laser; (2), (11) beam splitters; (3) glass prism; (4) gold film; (5) binding or another film; (6) aqueous solution (if necessary); (7) water (air) chamber; (8), (12) polarizers; (9) phase retarder; (10) mirror; (13) optical system, and (14) CCD camera.

the SPR phase upon system parameters (for example, optical thickness) can be used to improve the sensitivity of the SPR microscopy technique[16–18] and develop interferometric SPR imaging (ISPRI) with monoatomic thickness and micrometer spatial resolutions. For this, we combine a SPR interferometer[14] with a conventional SPR microscope[16] by an introduction of an additional reference beam, which interferes with the SPR signal beam.

An example of the ISPRI installation is depicted in Fig. 2. Here, a parallel beam of *p*-polarized radiation is divided to a signal and reference beams by a beam splitter (2). The signal beam is used for the SPR production in the Kretschmann prism arrangement.[6] It is directed at the SPR angle onto Au film (4) deposited on a glass prism (3). A thickness of the gold is selected to provide minimal reflected light intensity within the SPR dip (5%–10% of the incident light), when the phase jump is the most abrupt (in our conditions, the optimal thickness is about 50 nm). The gold film serves as one of the interferometer's mirrors. The light reflected from the film is directed to a second beam splitter (11), by which it is combined with the reference beam. After an enlargement by an optical system (13), an interference pattern is recorded by a charge coupled device (CCD) camera (14). The installation can work in the mode of the Zernike phase contrast, where two beams are parallel to each other, and the phase and amplitude of the reference beam are selected by the use of a phase retarder (9) and polarizers (8), (12) to visualize phase changes. It can also work in the fringe mode, where two beams interfere at some angle and phase changes result in bending and moving of the fringe structure. In both cases, information about the phase of the signal beam can be obtained from the spatial intensity distribution in the interference pattern. Here, the interference angle is an additional parameter, which is adjusted to achieve desired lateral resolution and sensitivity. Note that the installation can be easily transformed to a mode of the conventional amplitude SPR microscopy by blocking the reference beam. In our experiments, we analyze a response of the system when different films (including films of biological origin) are deposited on the gold.

Higher resolution of the ISPRI method over the conventional SPR microscopy can be seen from Figs. 3(a)–3(c), which show the images of an ultrathin droplet of a fatty acid on the gold film. The presence of the droplet can be easily detected in the phase contrast mode by an appropriate selection of the phase and intensity of the reference beam (a). In addition, the droplet produces a bending of the interference fringe structure in the fringe mode (b). However, the intensity SPR contrast for this droplet is lacking since the conventional SPR microscopy finds nothing at the droplet position (c). To get the latter image the reference beam of the interferometer was blocked and the installation was positioned at the angle of the maximal intensity contrast. It is evident that the improvement of the sensitivity can only be due to the phase jump behavior discussed earlier. Taking into account the phase variation due to the droplet presence, we can estimate the thickness of the droplet from calculated dependencies for the phase and intensity under SPR[11] ($h \sim 1$ A).

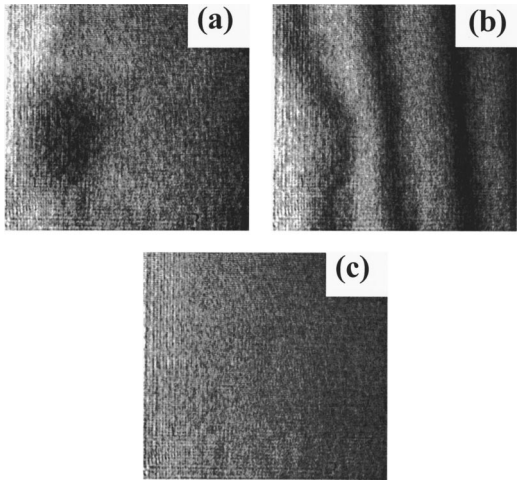

FIG. 3. The interferometric SPR images of a thin droplet of a fatty acid of 1 mm in diameter on a gold surface: (a) in the Zernike phase contrast mode; (b) in the fringe mode; and (c) in the amplitude SPR microscopy mode. All images represent measured raw data without an additional software processing.

The ISPRI scheme was found to provide a monoatomic thickness resolution. The presence of the edge of a 5-A-thick Si film on the gold surface (this thickness corresponds to three monoatomic Si layers) is easily detected by a distortion and broadening of the interference fringes in the region of the edge as shown in Fig. 4(a), while the amplitude SPR microscopy is not capable to resolve it, see Fig. 4(b).

Figure 5(a) presents responses of the phase-sensitive ISPRI (curve 1) and the amplitude-sensitive SPR microscope (2) to *in situ* reaction of gold with self-assembling thiol molecules dissolved in an aqueous solution. The reaction results in a formation of a superficial thiol layer on the gold. The process leads to a progressive change of the SPR conditions,

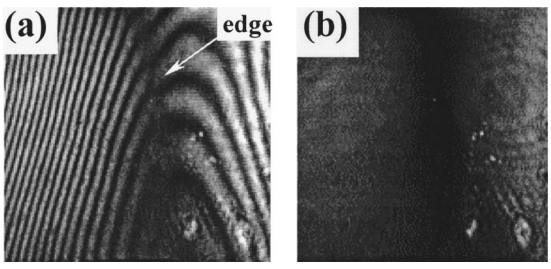

FIG. 4. The SPR images of the edge of a Si film with the thickness of 5 A deposited on the gold surface by a thermal evaporation: (a) in the fringe mode of the interferometric SPR imaging and (b) in the amplitude SPR microscopy mode.

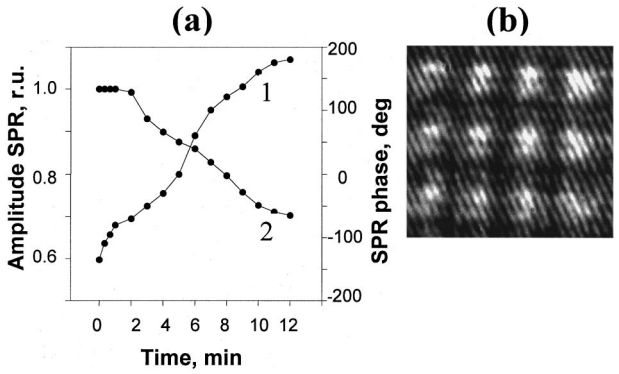

FIG. 5. (a) Temporal dependence for the phase (curve 1) and intensity (2) of the beam reflected under SPR for reaction of self-assembling thiol with gold. (b) The fringe mode interferometric SPR image of a Si test structure with the cell dimensions $100\times100\ \mu m^2$ and thickness of 2 nm.

which is accompanied by a change of the phase and intensity of reflected light. It follows from the figure that in contrast to the conventional SPR scheme, phase-sensitive ISPRI enables to observe initial stages of the reaction when the thiol layer on the gold is very thin.

Thus, taking an advantage of the Heaviside phase jumps the method of interferometric SPR imaging is able to detect objects and reactions that can not be resolved by the conventional SPR microscopy. There are two sources that contribute to the higher phase sensitivity of ISPRI. First, the maximal changes of the reflected electric field due to a thickness variation or a biochemical reaction occur at the minimum of the SPR curve, where the plasmon field that acts on tested medium is maximal. However, these changes affect only the phase of the reflected light and can not be seen by amplitude SPR. The phase contrast converts these phase changes into the amplitude ones. Second, the phase and the amplitude of the reference beam of the interferometer can be chosen to suppress the background light intensity without the degradation of signal. This serves to reduce the optical noise and to improve the signal-to-noise ratio.

It is known that SPR microscopy is unique in achieving a high sensitivity in measurements of a two dimensional (2D) distribution of a thickness of a studied film with a high lateral resolution (a subangstrom change itself of an average film thickness can be detected by a variety of another methods). Using phase peculiarities, interferometric SPR imaging can remarkably improve the thickness resolution of the 2D image of a studied film. ISPRI can be easily adapted for the solution of modern tasks of bio[19] and chemical[20] recognition, which require a combination of a high sensitivity with a fine spatial resolution over the sensitive film. In this case, the processing of a 2D interferometric image allows one to detect results of bio- or chemical interactions even though they occur in several film fragments or cells. In particular, the technique can be used in gene chips[21,22] for affinity reaction detection in an array and high throughput screening analyses,[23,24] which have to process simultaneously affinity arrays consisting of numerous (up to 10 000) identical cells. Figure 5(b) demonstrates the ISPRI fringe mode of compact affinity microarrays. A fringe movement inside a cell caused by a studied reaction provides the phase signal, while an intensity averaging over the fringe period yields the conventional amplitude (intensity) signal. It is important to note that dramatic changes of the SPR phase reveal themselves within a narrow dynamic range of variations of a measured parameter, near the dip of the SPR curve. To maintain the high phase sensitivity over a wide dynamic range, it is necessary to use a feedback control imposed on the light wavelength in order to keep the system parameter within the limits of fast phase changes.

In summary, we have discussed the topological property of phase and considered SPR as a prominent example of the Heaviside step-like phase behavior. We have shown that this jump can be applied to study ultrathin films and to improve existing bio and chemical sensors. Other optical systems with zero reflection or transmission, for example the Fabry–Perot interferometer or the Lummer–Gehrcke interferometer, can also be used to develop the interferometric imaging.

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