Metal-Dielectric-Graphene Hybrid Heterostructures with Enhanced Surface Plasmon Resonance Sensitivity Based on Amplitude and Phase Measurements

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Received: 29 September 2021 / Accepted: 29 December 2021 / Published online: 15 January 2022
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Abstract

Metal-dielectric-graphene hybrid heterostructures based on oxides Al_2O_3 , HfO_2 , and ZrO_2 as well as on complementary metal–oxide–semiconductor compatible dielectric Si_3N_4 covering plasmonic metals Cu and Ag have been fabricated and studied. We show that the characteristics of these heterostructures are important for surface plasmon resonance biosensing (such as minimum reflectivity, sharp phase changes, resonance full width at half minimum and resonance sensitivity to refractive index unit (RIU) changes) can be significantly improved by adding dielectric/graphene layers. We demonstrate maximum plasmon resonance spectral sensitivity of more than 30,000 nm/RIU for Cu/ Al_2O_3 (ZrO_2 , Si_3N_4), Ag/ Si_3N_4 bilayers and Cu/dielectric/graphene three-layers for near-infrared wavelengths. The sensitivities of the fabricated heterostructures were ~5–8 times higher than those of bare Cu or Ag thin films. We also found that the width of the plasmon resonance reflectivity curves can be reduced by adding dielectric/graphene layers. An unexpected blueshift of the plasmon resonance spectral position was observed after covering noble metals with high-index dielectric/graphene heterostructures. We suggest that the observed blueshift and a large enhancement of surface plasmon resonance sensitivity in metal-dielectric-graphene hybrid heterostructures are produced by stationary surface dipoles which generate a strong electric field concentrated at the very thin top dielectric/graphene layer.

Keywords Metal-dielectric-graphene hybrid heterostructures · Plasmon resonance biosensing · Amplitude and phase sensitivity · Surface dipoles · Electric field enhancement

Introduction

Surface plasmon resonance (SPR) has been extensively studied in the last three decades with focus placed on biosensing applications [1–4]. The main advantage of SPR biosensing is high raw sensitivity of SPR to variations of the refractive index (RI) of the medium covering the metal film that supports surface plasmon polaritons (SPP) [5–7]. In spite of extensive research efforts, SPR biosensing [4] of low

concentration of analytes with small sizes (typically less than 500 Da) remains a challenging task [3]. Raw sensitivity of SPR sensors depends mainly on the design parameters and a method of measurements (amplitude/phase interrogation, spectral/angular dependences). Recently, researchers proposed several approaches to improve raw SPR sensitivity by changing the structure of a SPR sensor. Lahav et al. [8, 9] suggested guided-wave SPR configuration, where a 10–15-nm high-refractive-index dielectric layer (Si) between a metal layer and an analyte was added to the conventional SPR scheme. The proposed by Lahav et al. [8, 9] configuration has two prominent advantages. The first advantage is that sensitivity of the suggested configuration was enhanced several times as compared to a SPR sensor without a dielectric layer (nearly four times improvement in angular sensitivity has been achieved by adding a 10 nm Si film to a conventional SPR sensor). The second advantage is that the stability of the metal layer was improved because the silicon served as a protection layer for the silver which

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normally suffers from corrosion. The drawbacks of the suggested material combination are an additional absorption of the added Si layer in visible and near IR ranges and the difficulty to achieve bio-functionalization of the dielectric layer necessary for biosensor selectivity. Another prospective way to significantly improve SPR raw sensitivity is based on a layered material platform that was proposed and optimised in [6, 10, 11]. In this case, a 2D atomic layered material is added to a metal SPR chip with an idea to achieve extremely deep plasmon SPR with almost zero reflection in layered material-protected metal SPR chips. It was established that the points of zero reflection provide extremely sharp phase changes [12] which can be used for extremely sensitive phase SPR biosensing [13]. Recently, phase-sensitive graphene-protected copper SPR chips were applied to rapid and sensitive detection of malaria which is a major tropical disease affecting approximately 500 million people and causing 1.5 to 2.7 million deaths every year [14]. It is important to note that in hybrid graphene–plasmonic configuration, the graphene layer plays a dual role. First, graphene protects plasmonic metals (such as, e.g., reactive Cu or Ag films) from oxidation during biosensing which often requires liquid environment accelerating corrosion. Second, graphene is used as a bio-functionalized surface that provides selectivity of biosensing. Overall, graphene–plasmonic structures displayed enhanced sensitivity as well as pronounced chemical stability and bio-functionality [6, 11, 14].

Other hybrid SPR heterostructures containing 2D atomic materials have been studied for RI sensing; e.g., a graphene/MoS₂-based heterostructure was investigated in Ref. [15]. Due to high values of optical constants of MoS₂, a stronger SPR excitation can be achieved in the noble-metal/MoS₂/graphene SPR chips. It was found that coating of a 45-nm Au thick film by 3-layer MoS₂ and a monolayer graphene reduces the width of the SPR curve and provides phase sensitivity enhancement about two orders of magnitude as compared to Au/graphene SPR systems [15]. To achieve the maximum sensitivity in this structure, materials and the number of transition metal dichalcogenide (TMD) layers have been optimized [16, 17]. It was found that adding several layers of TMDs on the top of noble metal films improves electric field enhancement at the sensing interface (graphene in this case) and leads to improved sensitivity. This was confirmed in works [18, 19] where silver films covered by thin (< 10 nm) dielectric layer with high refractive index were considered. It is worth noting that most of the works devoted to SPR sensitivity of noble-metal/TMD/graphene hybrid heterostructures were theoretical ones. This is connected with experimental difficulties in producing heterostructures with given numbers of high-quality TMD monolayers and graphene for SPR-sensing applications. These difficulties can be elevated by replacing the top 2D layer with a

reasonably thick metal layer; however, the sensitivity of the resonances would drop. To improve sensitivity in this case, one can use other geometries, e.g., metal–insulator–metal waveguides as proposed in [20].

The presence of an additional dielectric layer in a SPR structure can lead to complications connected with large electric fields induced in the layers. In our recent works [21–23], we have shown that electric double-layers (or ion traps) at the interfaces of metal–dielectric and dielectric–graphene can be easily formed. Due to this effect, it is possible to enhance the charge induced in graphene and hence to affect its properties. In a pioneering work, Agranovich et al. showed that the SPPs are strongly dependent on surface currents and charges present on the surfaces and interfaces [24]. These charges naturally occur in hybrid SPR heterostructures due to work-function considerations [18, 19] which lead to formation of a dipole layer at the interfaces [18, 25]. It could happen that frequencies of interface dipole oscillations would lie in the SPP frequency range. In this case, the presence of interface dipoles would strongly affect the SPR response [24, 26], and interface dipoles could produce a strong electric field enhancement in the sensing top layer that would lead to an ultrahigh sensitivity of the SPR-sensing system.

Here, we report a detailed study of hybrid heterostructures for SPR applications that include both thin layers of oxides and 2D layered materials. Namely, we consider noble-metal/dielectric/graphene heterostructures designed to achieve an improved raw SPR sensitivity to refractive index of environment and hence biosensing binding events. Both amplitude and phase interrogation SPR techniques [12, 27, 28] were evaluated. We study three-layer systems that combine plasmonic metal film Cu or Ag with a thin (~ 7 nm) dielectric film of a high refractive index such as Al₂O₃, HfO₂, ZrO₂ and Si₃N₄ and a graphene monolayer.

The improved SPR-sensing performances of these systems are provided by darkness (extremely low reflectivity at the minimum of a SPR curve), associated sharp phase changes and narrow full width at half minimum (FWHM) of the resonances. Our analysis reveals that the effective real and imaginary part of the dielectric permittivity plays an important role in determining the dispersion properties of SPP and spectral position and darkness of the SPR curve. We show that an optimization of the thicknesses of metal and dielectric films in such SPR chips can yield almost an order of magnitude gain of raw amplitude sensitivity as compared to the commercial gold SPR chips. In addition, copper and silver are inexpensive (compared to gold), have lower optical losses in the visible and NIR ranges, and are CMOS-compatible processes [6, 11]. Our work will be useful for researchers working with ultrasensitive label-free biosensing based on SPR platform.

Results and Discussion

Experimental Methods

Preparations of Noble Metal/Dielectric/Graphene SPR Chips and SPR Measurements

Copper and silver metal films were fabricated by electron-beam evaporation (see sect. “Materials and Methods”). Dielectric layers made of Al_2O_3 (HfO_2 , ZrO_2) were deposited by electron-beam evaporation without breaking the vacuum between the Ag (Cu) and dielectric layer depositions. For deposition of Si_3N_4 dielectric layers, we used the method of chemical vapor deposition (CVD) which allows one to achieve better morphology and hence better plasmonic characteristic of the ultimate devices. The thicknesses of metal and dielectric layers were chosen according to Fresnel simulations to realize the deepest SPR curves. Note that optimized (theoretically and experimentally) thicknesses of layers in the proposed trilayer metal/dielectric/graphene heterostructure are a Cu layer (40 nm) or Ag (45 nm) and a dielectric layer (7–8 nm). Metal films of chosen thicknesses yielded strongly enhanced electromagnetic fields on the top of heterostructures, while a high-refractive dielectric layer of a small thickness reduced the losses. A graphene monolayer significantly improved sensor stability and promoted new type of bio-functionalization as compared to gold SPR. We noticed that blue shift of SPR and enhancements of bio-sensitivity in the system are only significant when thickness of the dielectric layer is less than 10 nm. The bare quartz/ Al_2O_3 (HfO_2 , ZrO_2 , Si_3N_4) structures with thickness of dielectric 7–8 nm were also separately deposited and measured using ellipsometry. Their refractive indexes were extracted from angle and wavelength-dependent ellipsometric parameters with the help of the corresponding Cauchy functions and Fresnel fitting. To fabricate metal/dielectric/graphene samples, we transferred a monolayer of graphene

on the top of the bilayer heterostructure. A Turbadar–Kretschmann–Raether scheme of SPP excitation on planar interfaces (see Fig. 1) has been employed (see sect. “Materials and Methods”) [29–31]. In this scheme, the prism is placed on top of the glass substrate carrying metal/dielectric/graphene heterostructure, and excitation of SPPs happens at the far side of the metal-dielectric layers. The ellipsometric spectra were collected using an unfocused beam Woollam ellipsometer M-2000 with spot diameter of ~ 3.5 mm and the angle range of 45 – 75° . The optical data were recorded as a pair of ellipsometric parameters Ψ and Δ in the spectral range of 240–1700 nm with a wavelength step of ~ 1 nm. The parameter Ψ represents the ratio of Fresnel reflection amplitudes and Δ phase shift between p - and s -components of polarized light [11, 27, 28]. The ellipsometric parameters are connected to the Fresnel amplitude reflection coefficients r_p and r_s for the p - and s -polarized light, respectively, as $\tan(\Psi)\exp(i\Delta) = \frac{r_p}{r_s}$. The excitation of SPR at the surface of noble metal/dielectric/graphene was observed as a strong dip in Ψ accompanied by very sharp changes of Δ that happens for a specific combination of angle of incidence and light wavelength [6, 11, 28, 32].

Experimental Results

In Fig. 2, we plot the SPR spectral curves for the Cu(Ag)/ Al_2O_3 (HfO_2 , Si_3N_4 , ZrO_2) heterostructures with and without the top graphene monolayer. Monolayer nature of CVD graphene transferred on the top of the dielectric was checked by the Raman spectroscopy (see, Fig. 1 of Supplementary Information (SI)). For both metals Cu and Ag, the position of the sharp dip of the SPR curves shifts to smaller wavelengths (blueshifts) in the presence of dielectric layer except for the case of hafnia (HfO_2). As expected, the spectral width of the SPR reflectance dip at half minimum, FWHM or $\Delta\lambda_R$, is larger for bilayers based

Fig. 1 Copper(silver)-dielectric-graphene hybrid nanostructures with enhanced sensitivity. **a** Schematic of electron–hole (e–h) pairs production as dipole transitions at the interfaces of copper–dielectric and

dielectric–graphene interfaces. **b** Schematic diagram of SPR sensor for copper–dielectric–graphene hybrid nanostructures with enhanced EM field due to SP propagation and interface dipoles emission

on Cu films (Fig. 2) and smaller for Ag heterostructures. Adding a thin layer of dielectrics to SPR structure does not only shifts the SPR position but also changes the FWHM. For optimized structures, the FWHM of SPR resonances obtained here in Cu(Ag)/Al₂O₃(HfO₂, Si₃N₄, ZrO₂)/graphene heterostructures is less than about $\Delta\lambda_R \sim 28$ nm. This is smaller than typical values observed for the SPR on the Cu-air interface (Figs. 2, S.2, S.3, S.4). It is worth noting that the FWHM of SPR reflectance dip is twice as large as ~ 50 nm for Au films [26].

Fig. 2 Strong and narrow SPR of copper(silver)-dielectric-graphene hybrid nanostructures (coupling prism, $n=1.5$). **a** Ellipsometric parameters Ψ (amplitude) of the SPR curve of bilayer Cu (40 nm)/dielectric (7 nm). **b** Ellipsometric parameters Ψ of the SPR curve of

Fig. 3 SPR biosensing of copper-dielectric hybrid nanostructures (coupling prism, $n=1.8$). **a, b** Change of spectral position $\Psi_{\min}(\lambda)$ and corresponding change (jump) of phase ($\delta\Delta$) as a function of the refractive index of water-glycerol solution for bilayer Cu (40 nm)/Al₂O₃(7 nm). **c, d** Change of spectral position $\Psi_{\min}(\lambda)$ and corresponding jump of phase ($\delta\Delta$) as a function of the refractive index of water-glycerol solution for bilayer Cu (40 nm)/Si₃N₄(8 nm). **e, f** Change of spectral position $\Psi_{\min}(\lambda)$ and corresponding jump of phase ($\delta\Delta$) as a function of the refractive index of water-glycerol solution for bilayer Cu (40 nm)/ZrO₂(7 nm)

bilayer Ag (45 nm)/dielectric (7 nm). **c, d** Ellipsometric parameters Ψ and p -polarised reflectivity R_p of the SPR curve of three layers Cu(Ag)/dielectric/graphene

Figure 2c, d show the SPR reflectance spectra $\Psi(\lambda)$ and $R_p(\lambda)$ for metal/dielectric/graphene heterostructures. Graphene induces a small spectral shift of SPR at ~ 10 nm

for hybrid heterostructures based on Cu and ~ 30 nm for heterostructures based on Ag. The measured p -polarised reflection spectra in Fig. 2d demonstrate very small values

Fig. 4 SPR biosensing of silver-dielectric hybrid nanostructures (coupling prism, $n=1.5$). **a, b** Change of spectral position $\Psi_{\min}(\lambda)$ and corresponding change of phase ($\delta\Delta$) as a function of the refractive index of water-glycerol solution for bilayer Ag (45 nm)/Al₂O₃(7 nm). **c, d** Change of spectral position $\Psi_{\min}(\lambda)$ and corresponding jump of

phase ($\delta\Delta$) as a function of the refractive index of water-glycerol solution for bilayer Ag (45 nm)/Si₃N₄ (8 nm). **e, f** High spectral sensitivity evaluated from shift of SPR wavelength ($\delta\lambda_{\min}$) for Ψ dependences versus of the refractive index of water-glycerol solution for bilayer Cu-dielectric (**e**) and for bilayer Ag-dielectric (**f**)

(approximately zero) of reflection at the dip of the SPR curve, $R_{p,\min}$ and the narrow FWHM $\approx 30\text{--}35$ nm especially for Cu/ZrO₂/graphene and Ag/Si₃N₄/graphene hybrid heterostructures. Remarkably, such small FWHM were not previously observed for Cu or Ag SPR chips. These measurements confirm that graphene monolayer on the top of noble-metal/dielectric heterostructures can improve SPR characteristics. The quality factor Q of the SPR ($Q = \lambda_R / \Delta\lambda_R$, where λ_R is the resonance wavelength corresponding to the SPR reflection minimum and $\Delta\lambda_R$ is FWHM of the resonance curve) was maximal $Q \sim 50$ for the optimal Ag/Al₂O₃ heterostructure and minimal $Q \sim 21$ for optimized Cu/Si₃N₄ structures, as can be estimated from the ellipsometric $\Psi(\lambda)$ SPR curves (Fig. 2). These characteristics are better than those observed for pure Au, Ag and Cu films with SPR in the green–red wavelength range [6, 11, 33, 34]. Such behaviour of the SPR spectral position and width indicates that the propagation characteristics of SPPs are very sensitive to the choice of metal and dielectric in hybrid heterostructures.

At the next stage, we have tested raw SPR sensitivity of the fabricated plasmonic metal/dielectric/graphene heterostructures to changes of RI of water-glycerol solutions placed at the top of SPR chip; see schematic, Fig. 1b. We used two types of interrogation: (i) the amplitude interrogation method based on the ellipsometric parameter $\Psi(\lambda)$, where the shift of the reflectance minimum is determined at a fixed angle of incidence; (ii) the phase interrogation method, where changes of the ellipsometric phase $\Delta(\lambda)$ are measured (Figs. 3, 4, and 5). For the amplitude interrogation method, an intensity of reflected light at SPRs minimum for different Cu(Ag)/Al₂O₃(Si₃N₄, ZrO₂) heterostructures is close to zero for water/glycerol mixture environment. The wavelengths of the SPR spectral position were extracted and plotted in Fig. 4e, f where we can see that the SPR wavelength shifts almost linearly with a change in RI of the surrounding medium. The slope in Fig. 4e, f gives the RI detection sensitivity. Therefore, we can introduce a sensitivity parameter S that describes the resonance wavelength shift per refractive index unit (nm/RIU) and can be expressed as $S = d\lambda/dn$ [2, 35, 36]. Note that, for extracting sensitivity of SPR to RI, we have used ellipsometry methods which are immune to many sources of noise since they measure and fit the ratio of the reflection coefficients and phase difference which are extremely sensitive to small changes of RI. We showed that narrow and deep SPRs can be tuned from the near IR (~ 900 nm) to the mid-IR (~ 1600 nm) just by altering the environment's RI (water/glycerol mixture). The linear fit yields a very high spectral sensitivity of $S = d\lambda/dn \sim 38,000$ nm/RIU for Cu/Al₂O₃ bilayers (without graphene); see Fig. 4e–f and Table 1. This sensitivity can be estimated from the resonance wavelength shift of $d\lambda \sim 220$ nm at the minimal detected changes of $dn = 0.00577$

as shown in Fig. S.2. It is worth mentioning that, for all investigated samples, we have repeated SPR-sensing experiments three times to precisely evaluate the amplitude and phase changes and confirm a high sensitivity.

Near-infrared SPRs for the Ag/Al₂O₃(Si₃N₄) bilayers in the water-glycerol solutions exhibit broader FWHM than ones in air. The highest SPR sensitivity of $S = 30,900$ nm/RIU was recorded for Ag (45 nm)/Si₃N₄ (8 nm) hybrid structure (Fig. 4a–d and Table 1, Fig. S.2). The abrupt phase $\Delta(\lambda)$ changes are observed at the resonance due to low value of reflection at the resonance minimum. Note, that if investigated samples do not exhibit complete darkness at the SPR wavelengths, the ellipsometric phase $\Delta(\lambda)$ changes are not pronounced. Similar to the amplitude ellipsometric characteristic $\Psi(\lambda)$, the phase parameter $\Delta(\lambda)$ exhibits linear dependence as a function of RI at a wavelength where phase jumps occur (Figs. 3 and 4). The spectral widths of the experimentally measured phase $\Delta(\lambda)$ are hard to define due to the drastic changes within the very narrow spectral range and the limited spectral resolution of the Woollam ellipsometer used in the experiments (~ 1 nm). Detailed analysis of the data shown in Figs. 3 and 4 suggests that the most sensitive heterostructure was Cu/Al₂O₃. It is worth noting that phase changes for Ag/Al₂O₃(Si₃N₄) SPR heterostructure are hysteretic as a function of RI (Fig. 4b, d). Generally, a phase response of the studied SPR heterostructures demonstrates noticeably strong changes for extremely close values of external parameters.

Finally, Fig. 5a–g show changes of the ellipsometric parameters $\Psi(\lambda)$ and $\Delta(\lambda)$ for the metal/dielectric/graphene heterostructures measured in water-glycerol solutions. As one can see from Fig. 5, the SPR position shifts to longer wavelengths while the resonance widths $\Delta\lambda_R$ is slightly increased at an increase of the RI of the top liquid. It is interesting to note that the sharp changes of phase $\Delta(\lambda)$ are more significant than that of the amplitude $\Psi(\lambda)$ at the resonance wavelengths. The changes in the phase $\delta\Delta(\lambda)$ are more than 250° for the refractive index change of 0.0012 RIU, which yields the phase sensitivity of $\sim 1.7 \times 10^5$ /RIU for the case of Cu/Al₂O₃/graphene heterostructures (Fig. 5). Overall, among all the optimised sensing trilayer SPR chips, 40-nm Cu film with thin Al₂O₃ or Si₃N₄ dielectric layers (of the thickness 7–8 nm) covered by graphene monolayer provided the best sensing configuration with significant amplitude and phase sensitivities. At the same time, SPR sensitivity of bilayers Cu/Al₂O₃ was even better due to non-ideal properties of transferred graphene; see Raman spectra shown in Figure S.1.

The amplitude figure of merit (FOM) of SPR chips, defined as sensitivity S divided by the resonance linewidth FWHM, $\Delta\lambda_R$ [2, 34, 35], can be written as $FOM = S/\Delta\lambda_R$. For the best of our bilayer metal/oxide heterostructures, FOM was at the level of $FOM = 590$ for Cu (40 nm)/Al₂O₃

Fig. 5 SPR biosensing of Cu(Ag)/Al₂O₃(HfO₂,Si₃N₄,ZrO₂)/graphene hybrid nanostructures (coupling prism, $n = 1.8$). **a, b** Change of spectral position $\Psi_{\min}(\lambda)$ and corresponding jump of phase ($\delta\Delta$) as a function of the refractive index of water-glycerol solution for three layers Cu (40 nm)/Al₂O₃(7 nm)/graphene. **c, d** Change of spectral position $\Psi_{\min}(\lambda)$ and corresponding jump of phase ($\delta\Delta$) as a function of the refractive index of water-glycerol solution for three layers Cu (40 nm)/Si₃N₄(8 nm)/graphene. **e, f** Change of spectral position $\Psi_{\min}(\lambda)$ and corresponding jump of phase ($\delta\Delta$) as a function of the refractive index of water-glycerol solution for three layers Ag (45 nm)/Si₃N₄(8 nm)/graphene. **g, h** Change of spectral position $\Psi_{\min}(\lambda)$ and corresponding jump of phase ($\delta\Delta$) as a function of the refractive index of water-glycerol solution for three layers Cu (40 nm)/ZrO₂ (7 nm)/graphene

(7 nm) and $FOM = 690$ for Ag (45 nm)/Si₃N₄ (8 nm) sandwiches; see Table 1 (these numbers were obtained using the sensitivity S of heterostructures and FWHM of plasmonic resonances $\Delta\lambda_R$, which were $S \sim 38,000$ nm/RIU and $\Delta\lambda_R \approx 65$ nm in water for Cu/Al₂O₃ bilayer and $S \sim 31,000$ nm/RIU and $\Delta\lambda_R \approx 45$ nm for Ag/Si₃N₄ bilayer). It is at the same level as $FOM = 590$, the highest FOM that was previously obtained for complicated hyperbolic metamaterials, [37] and about 5 times higher than for standard Au-based sensors [33]. When covered by graphene, the sensing properties of metal/oxide bilayers change (see Fig. 5 and Table 1). The amplitude FOM was 450 for the most sensitive Cu (40 nm)/Al₂O₃ (7 nm)/graphene heterostructure (see Table 1). At the same time, due to the larger darkness of SPR, the phase sensitivity observed was $\sim 10^5$ °/RIU for the studied heterostructures which is one order of magnitude higher than that of the conventional Au thin film with 50 nm thickness (which is usually $\sim 10^4$ °/RIU, although it could be improved for some dedicated systems [38, 39]). Combining the amplitude and phase detection methods, the proposed biosensor hybrid system can maintain the unique advantages in terms of both high amplitude sensitivity of $> 30,000$ nm/RIU and the phase detection limit at the level of 10^{-8} RIU at the same time. The enhancement of the amplitude sensitivity for the studied

plasmonic metal/dielectric/graphene heterostructures was about 5–8 times as compared with SPR amplitude sensitivity based on bare Cu or Ag thin films. Note also that the maximum of RI sensitivity of designed Cu(Ag)/dielectric/graphene nanostructures is more than one order of magnitude higher than that of a highly sensitive sensor-based localised surface plasmon resonances (~ 2000 nm/RIU) theoretically discussed in [40]. This shows that the proposed platform of heterostructure biosensors could outperform conventional SPR (as well as LSPR) chips by almost an order of magnitude by using the amplitude and phase interrogations.

Discussion

Dielectric Function of the Hybrid Plasmonic Nanostructures

From experimental results, we can see that thin dielectric or dielectric/graphene layers added to the SPR chip can strongly impacts the optical properties of SPR devices. Normally, the SPR chips with added heterostructures are modelled with the help of Fresnel theory [41]. However, when thickness of added layers becomes small, then, the surface effects can play an important role, and the optical constants of thin layers could be different from those of bulk materials. For example, graphene has optical constants different from those of bulk graphite [42] or optical properties of MoS₂ monolayers can be different from those of bulk MoS₂ [43]. Our modelling of the ellipsometric characteristic $\Psi(\lambda)$ (p - and s -polarised reflections) based on the Fresnel approach [41] revealed that the lowest value of minima reflectivity $\Psi(\lambda)$ are redshifted when we add the different dielectric layers of thickness 7–8 nm on top of plasmonic Cu film (Figure S.3). This result is in contradiction with the experimental dependences which demonstrate the unexpected blueshift of SPR for high-index

Table 1 Amplitude and phase sensitivities of SPR for noble metal/dielectric/graphene hybrid nanostructures based on spectro-ellipsometric measurements: $\Psi(\lambda)$ and $\Delta(\lambda)$. SPR sensors performed on Cu(Ag)/dielectric/graphene are relatively cheap, stable, reproducible, and high-quality plasmonic material with strong sensitivity $S > 30,000$ nm/RIU and figure of merit $FOM \approx 400$ –690 (1/RIU)

Sample	Amplitude spectral sensitivity: $S = d\lambda/dn$ (nm/RIU)	FOM, ratio: $FOM = S/\Delta\lambda_R$ (1/RIU) in water	Phase signal Δ per 10^{-3} RIU (°)
Cu@Al ₂ O ₃	38,500	590	52.0
Cu@Si ₃ N ₄	32,900	470	49.5
Cu@HfO ₂	5900	110	41
Cu@ZrO ₂	37,500	430	50
Ag@Al ₂ O ₃	19,200	280	46
Ag@Si ₃ N ₄	30,900	690	49
Ag@HfO ₂	6480	310	45
Cu@Al ₂ O ₃ @graphene	28,000	450	51
Cu@Si ₃ N ₄ @graphene	30,200	350	48
Ag@Si ₃ N ₄ @graphene	24,500	360	47
Cu@ZrO ₂ @graphene	25,500	430	49

Fig. 6 Dielectric function of Cu(Ag)/Al₂O₃(HfO₂, Si₃N₄, ZrO₂)/graphene hybrid nanostructures. **a, b** The effective real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function for Cu (45 nm) and bilayer Cu (40 nm)/dielectric (7 nm). **c, d** The effective real (ϵ_1) and imagi-

nary (ϵ_2) parts of the dielectric function for Ag (45 nm) and bilayer Ag (45 nm)/dielectric (7 nm). **e, f** The effective real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function for three layers Cu/dielectric/graphene

dielectric covering; see Fig. 2. Moreover, we have found that the width of the experimental SPR reflectivity curves could be significantly reduced by combining noble metal and a thin dielectric layer (< 10 nm) in contrast to the Fresnel theory of SPR. The redshift of SPR of plasmonic Cu film in hybrid nanostructures with a HfO_2 top layer as well as the blueshift of SPR for other bilayers ($\text{Cu}/\text{Al}_2\text{O}_3$, Si_3N_4 , ZrO_2) can be correlated with electronic states and morphology of dielectric surface. In recent work [21], we have checked stoichiometry of different oxides deposited by electron-beam evaporation on the top of a Cu thin film using X-ray photoelectron spectroscopy and found that density of oxygen vacancies in HfO_2 layer is much larger than that in Al_2O_3 . In addition, the surface roughness of deposited HfO_2 films was found to be the largest (Fig. S.5). We suggest that non-stoichiometric nature of deposited hafnia together with higher surface roughness resulted in the observed redshifts for Cu/HfO_2 hybrid nanostructures.

Knowing the complex dielectric function of the SPR chip covered with thin films and using an ingenious approach developed by Abeles [44], we can evaluate an important parameter of the problem: SPP propagation length (L_{SPP}). According to [44], the L_{SPP} is inversely proportional to the SPR minimum width and can be estimated as $L_{\text{SPP}} \sim \varepsilon_{1,\text{eff}}^2 / \varepsilon_{2,\text{eff}}$ (where $\varepsilon_{1,\text{eff}}$ and $\varepsilon_{2,\text{eff}}$, in our case, are the effective real and imaginary part of the dielectric function of metal/dielectric-graphene nanostructure). Hence, to achieve larger L_{SPP} , one needs a large real part of metal-dielectric constant, $\varepsilon_{1,\text{eff}}$, and a small imaginary component, $\varepsilon_{2,\text{eff}}$ (larger L_{SPP} indicates that the designed structures have higher transfer efficiency from the incident light to the SPR energy, leading to a stronger SPR excitation and a sharper phase change resulting in enhancement of RIU sensitivity). Using the measured ellipsometric functions $\Psi(\lambda)$ and $\Delta(\lambda)$, we can reconstruct the effective real $\varepsilon_{1,\text{eff}}$ and imaginary part $\varepsilon_{2,\text{eff}}$ of the dielectric function of metal/dielectric-graphene nanostructure [41, 45]. To do so, we consider bilayer or three layers stack as single effective (homogenise) layer. This approach only works for films with total thickness satisfying the condition $kd \ll 1$ (where k is wave vector of free space light and d is thickness of dielectric/graphene layers) [46]. This assumption is obviously valid for dielectric or dielectric/graphene layers which are thinner than the skin depth of noble metal (< 25 nm) on the probing wavelength (~ 600 nm) [47]. The resulting effective real and imaginary parts of the dielectric function ($\varepsilon_{\text{eff}} = \varepsilon_{1,\text{eff}} + i\varepsilon_{2,\text{eff}}$) of different $\text{Cu}(\text{Ag})/\text{dielectric}/\text{graphene}$ nanostructures are shown in Fig. 6.

Inspection of the $\varepsilon_{1,\text{eff}}$ demonstrates that, for Cu- and Ag-based hybrid nanostructures, $\varepsilon_{1,\text{eff}}$ are the smooth monotonic functions, which can be approximated by Drude permittivity in the red part of visible and the IR ranges. The behaviour of

the $\varepsilon_{2,\text{eff}}$ is more complicated: it reaches the minimum at λ_{min} (interband transitions), and then for $\lambda > \lambda_{\text{min}}$, it grows and starts to follow Drude dependence [45, 47]. Note that $\text{Cu}(\text{Ag})/\text{dielectric}/\text{graphene}$ hybrid nanostructures show smaller values of the $\varepsilon_{1,\text{eff}}$ and $\varepsilon_{2,\text{eff}}$ functions in near IR region as compared to pure $\text{Cu}(\text{Ag})$ plasmonic films. Surface roughness and grain size can contribute to an increase of the imaginary part of the dielectric function $\varepsilon_{2,\text{eff}}$ over the intrinsic bulk value [47]. The surface roughness of the $\text{Cu}(\text{Ag})/\text{dielectric}$ bilayers on glass substrate was measured using an atomic force microscope (AFM) and is shown in Figure S.5. It is worth noting that $\text{Cu}/\text{dielectric}$ heterostructures maintain smoother surface morphology (root mean square roughness (RMSR) changes from 1 to 2 nm) as compared to $\text{Ag}/\text{dielectric}$ films (RMSR ~ 3 –4 nm). The minimal RMSR of 1.2–1.3 nm was measured for $\text{Cu}/\text{Al}_2\text{O}_3(\text{ZrO}_2)$ bilayers which also yielded in the highest biosensitivity. Moreover, the significant increase of RMSR for Cu/HfO_2 bilayer confirms the fact that the morphology of surface can significantly reduce SPR sensitivity. Comparison of the $\varepsilon_{\text{eff}} = \varepsilon_{1,\text{eff}} + i\varepsilon_{2,\text{eff}}$ function for different $\text{Cu}(\text{Ag})/\text{dielectric}/\text{graphene}$ nanostructures (Fig. 6) and amplitude sensitivity (Figs. 3, 4, and 5) reveals strong correlation between a small value of the imaginary part of effective permittivity $\varepsilon_{2,\text{eff}}$ and large spectral sensitivity of SPR, $S = d\lambda/dn$. Note that SPR exhibits much lower FWHM $\Delta\lambda_R$ and higher FOM in the case of the higher slope $d\varepsilon_{1,\text{eff}}/d\lambda$ and smaller $\varepsilon_{2,\text{eff}}$ according to equation [48]: $\Delta\lambda_R = 4\varepsilon_{2,\text{eff}} / |d\varepsilon_{1,\text{eff}}/d\lambda|$. By optimizing the parameters of the $\text{Cu}(\text{Ag})/\text{dielectric}/\text{graphene}$ hybrid heterostructures, we can balance the optical absorption efficiencies and the electron losses ($\varepsilon_{2,\text{eff}}$) at the plasmonic resonance condition.

Interface Dipole Contribution in the Resulting Plasmonic Field

To explain the significant blueshift of the SPR spectral position for different $\text{Cu}(\text{Ag})/\text{dielectric}$ heterostructures in comparison to the pure $\text{Cu}(\text{Ag})$ films (except of HfO_2 oxide) (Figs. 2 and S.3, S.4), we consider the existence of a transition layer on the reflecting surface of the interfaces [49]. Sivukhin [49] was first to introduce the surface polarizabilities of thin films, produced either by lattice defects, atoms in excess of stoichiometry or, even in the case of ideal lattice, by differences in the intermolecular interaction and symmetry of the internal field. In this scenario, an infinitely thin layer, placed on the surface of the thin film, provides the dipole-moment surface densities which contribute to the polarised reflection [49]. We can also assume the significant impact of the interface dipoles on the properties of propagating SPPs for $\text{Cu}(\text{Ag})$ -high-index dielectric heterostructures (Fig. 1a, b). In the modern theoretical description, the SPR frequency is modified by introducing the complex Feibelman frequency-dependent parameters $d_{\parallel,\perp}$ to the Fresnel approach

according to [50–54]: $\omega_{SPR} = \omega_{SPR}^0 \sqrt{1 - kd_{\perp} + kd_{\parallel}}$, where ω_{SPR}^0 is the classical SPR frequency for pure noble metal film and k is the wavevector. Note that the Feibelman d_{II} parameter is usually small and vanishes for locally uncharged surface while $d_{\perp}$ can strongly impact the nonlocal correction to the SPP dispersion [53, 54]. Considering the $d_{\perp}$ parameter, we can conclude that, if $\text{Re}(d_{\perp}) < 0$, the SPR will be blueshifted while when $\text{Re}(d_{\perp}) > 0$ the resonance redshifted [54]. Moreover, the value of $\text{Im}(d_{\perp})$ can contribute to the narrowing/broadening of the SPR. Narrower resonances appear due to collective contribution in plasmonic resonance from assemblies of interfaces dipoles—in rough analogy of the collective dipole-like resonances from arrays ordered nanoparticles [2, 55]. Note that the magnitude of Feibelman $d_{II,\perp}$ parameters at the interface noble metal-dielectric are a few times higher than those at metal-air [53, 54]. Agranovich [24, 26] stressed that the appearance of microscopic surface excitons (interface dipoles in our case) causes the polarizability of the dielectric transition layer in the direction perpendicular to the separation boundary (interface) between the media. It could happen that the frequency of the microscopic surface exciton at ions falls into the surface-polariton band significantly affecting the SPP spectrum [24]. Note that the plasmon energies are found to increase with decreasing particle diameter for Si and SnO_x nanoparticles [56]. These energy shifts are related to the change of the dielectric bandgap energy of the semiconductor due to quantum size effects [56].

In addition, electron transfer due to the work-function difference between different layers and noble metals Cu (Ag) can promote a large electric field enhancement at the sensing interface and thus leading to higher sensitivity of the biosensor. It is worth noting that the work function of Cu (~ 5.22 eV) [25, 57] is higher than that of dielectrics Al_2O_3 (2.73 eV), HfO_2 (2.47 eV) and ZrO_2 (2.3 eV) [18]. Due to this, the successful transfer of electrons from dielectric/graphene hybrid layers to Cu film could occur under optical excitation. The dimension scale of such electrons transfers extends beyond the Thomas–Fermi (TF) screening length (the characteristic length $L_c = v_F/\omega$, where v_F is the Fermi velocity of electrons and ω is a light frequency). For standard values of about $v_F \sim 1.4 \times 10^6$ m/s, the resulting wavevector mismatch is on the scale of $\Delta k \sim L_c^{-1}$ and it is about 2 nm^{-1} for noble metals at 600 nm (~ 2 eV photon energy), and it is much larger than wavevector of the electromagnetic wave [58]. This estimation confirms that only at the interfaces can form (e–h) pairs, creating dipoles. The in-plane SPP propagation can strongly couple with the out-of-plane interface dipoles emission, as illustrated in Fig. 1a, b. This process is insignificant at a metal-low-index interface [17, 18] due to the high barrier; however, it could be large at a metal-high-index interface and could lead to intensified

energy of surface plasmon and narrowed absorption spectrum [18, 19]. This process could also promote larger electric field enhancement at the sensing interface thereby resulting in a higher SPR sensitivity to the target analytes.

Modelling of the SPR in the Plasmonic Heterostructures

To calculate the optical properties of the studied plasmonic metal/dielectric/graphene heterostructures, we introduced the Feibelman $d_{II,\perp}$ parameters approach [18, 51–54] for the Fresnel equations of reflection/transmission of incident light from a planar Cu(Ag)/dielectric/graphene interface [41]. The core idea underlying Feibelman $d_{II,\perp}$ parameters is an interface dipole expansion. In our modelling, we have only considered the changes of p -polarised reflectivity coefficients by introducing the Feibelman $d_{\perp}$ parameter in the standard matrix calculation [41]. The real and imaginary parts of $d_{\perp}$ were chosen from the best fit to our data. We set $\text{Re}(d_{\perp}) = -(0.15 - 0.17)$ for Al_2O_3 , Si_3N_4 , and ZrO_2 dielectrics in our calculation. The imaginary part was chosen to be $\text{Im}(d_{\perp}) \approx -0.1$. In Figure S.6, we plot the ellipsometric parameter $\Psi(\lambda)$ as a function of wavelength for all the dielectrics and reveal the blueshift SPRs which agrees with experimental dependences (Fig. 2). These results demonstrate that the suggested approach is suitable for the use in numerical modelling of complex heterostructures made of noble metals and high-index dielectrics/graphene layers and thus can predict an ultrahigh sensitivity of the SPR-sensing devices.

Conclusions

We have engineered a SPR-sensing hybrid heterostructures based on noble-metal/dielectric/graphene layers to achieve significant amplitude and phase sensitivity improvement of SPR sensing. The suggested planar noble metal/dielectric/graphene heterostructures possess high sensitivity owing to strong light-matter interaction region on the top of a graphene monolayer and could provide a simple and cost-effective solution for a label-free biosensing platform. We have shown the lower reflectivity values in SPR minimum for the noble-metal/dielectric/graphene heterostructures as well as high SPR raw biosensitivity and sharper phase changes at the resonance minimum. We have found that the highest spectral sensitivities for the studied system were observed for Cu/ Al_2O_3 and Cu/ ZrO_2 heterostructures (with and without graphene) which were around 38,000 nm/RIU and possessed the *FOM* of 420–590. The phase sensitivity of this system is increased by more than one order of magnitude as compared to gold SPR platform. The sensitivity enhancement is due to concentration of electromagnetic energy of plasmonic waves on the top of

dielectric/graphene layers. We suggested the mechanism of additional electric field enhancement at the sensing interface connected with creation of stationary surface dipoles at the interfaces between metals and dielectrics. This finding will be important for understanding and designing nanoplasmonic devices that utilize noble metals and high-index dielectrics/graphene layers with an idea to achieve ultrahigh sensitivity of SPR-sensing devices.

Materials and Methods

Sample Preparation

For the noble metal (Ag or Cu) deposition, we use electron-beam evaporation and strictly follow the same procedure all the time. Our deposition rate is controlled precisely at $1.0\text{ }^{\circ}\text{A s}^{-1}$ and the base pressure is 1.0×10^{-6} torr. Growth of the metal film was monitored by a calibrated quartz microbalance (CQM). Adhesive layer was chosen thin Cr (1.5 nm) film deposited on clean glass substrates by electron-beam evaporation. Then, on top of metallic (Ag or Cu) layer was evaporated dielectric (Al_2O_3 or HfO_2 , ZrO_2) using same technology process. Note that we did not break the vacuum between the Ag (Cu) and dielectric Al_2O_3 (HfO_2 , ZrO_2) deposition. This guarantees no oxidized layer formation on the Ag (Cu) surface. When we have used CVD to grow the Si_3N_4 dielectric, the exposure time of the already evaporated Ag and Cu films is at most 1–2 h in the ambient cleanroom environment. There is no sign showing any of our experimental results to be related to oxidize Ag (Cu) surfaces.

To fabricate Cu(Ag)/dielectric/graphene samples, we transferred single-layer graphene (SLG) on top of the bilayer nanostructure. The process of CVD graphene transferring consists from the following steps: (i) a monolayer of graphene on Cu foil substrate and acquired from 2D semiconductors was spin-coated with a poly(methyl methacrylate) (PMMA) resist for support. (ii) The copper substrate was etched in a solution of ammonium persulfate, and the floating membrane was cleaned in a subsequent bath of deionized water. Next, the PMMA/graphene films on the scotch type were fished for transfer procedure. (iii) The resulting monolayer of graphene was transferred on top of Cu(Ag)/dielectric structure using the standard dry-transfer technique as described in [43]. (iv) Finally, after drying overnight, the PMMA layer was removed by soaking in acetone.

Raman Confirmation

We used CVD method for large-area SLG preparation and single layer of the graphene transferred on the bilayer was confirmed by Raman spectroscopy (see Figure S.1,

Supporting Information). Raman spectra of CVD graphene transferred on top of dielectric thin film were recorded with a Witec confocal spectrometer at the excitation wavelength of 514.5 nm.

Morphology Testing

The surface morphology and the root mean square (RMS) surface roughness of deposited films were characterized by atomic force microscopy (AFM) (Nanoscope V with Dimension 3100). The samples were scanned by AFM using tapping mode, typically over a $5\text{-}\mu\text{m}^2$ area at a tip velocity of $1\text{ }\mu\text{m/s}$ and a corresponding scan rate of 1 Hz. Nanoscope software was utilized to analyse the images and extract the RMS.

Ellipsometric Measurements of the SPR Characteristics for Noble Metal-Dielectric Bilayers

Spectroscopic ellipsometry measurements are performed to check the sensitivity of SPR to refractive index, which further helps determine the corresponding wavelength for maximum sensitivity. Together with standard ellipsometric method, we have also employed recently developed method of total internal reflection ellipsometry (TIRE) which represents a very successful combination of the spectroscopic ellipsometry instrumentation with the Turbador–Kretschmann–Raether type surface plasmon resonance geometry of the experiment [29–31, 44, 45]. The obvious advantages of the TIRE method are as follows: (i) a possibility of measurements of both the amplitude (Ψ) and phase (Δ) related parameters and (ii) the separation of the light beam pass from the investigated medium. For TIRE measurements, the most common Kretschmann configuration of SPR ellipsometry was realized and shown schematically in Fig. 1. The SPR ellipsometry set-up used in our experiment is based on the commercially available variable angle spectroscopic ellipsometry (VASE) from J.A. Woolam Company (USA) equipped with a 45° (or 60°) glass prism and home-built micro-fluidic flow cell. The glass slide is brought into optical contact to the glass prism through the index matching fluid. The investigated incident angles range $\varphi = 45\text{--}75^\circ$ were near the surface plasmon resonance angle for TIRE. The state of polarization can be described in terms of two ellipsometric parameters Ψ and Δ , which are defined as $r_p/r_s = \tan \Psi \exp(i\Delta)$ (where $r_p = |E_p/E_i|$ and $r_s = |E_s/E_i|$ are the Fresnel reflection coefficients for light polarization parallel (r_p), and perpendicular (r_s) to the plane of incidence, E_i denotes the electrical field of the incoming light) contain information for both p - and s -polarized light components reflected from the sample surface. In addition to ellipsometric parameters Ψ and Δ , the ellipsometer allowed

us to separately measure $R_p = |r_p|^2$ and $R_s = |r_s|^2$, the intensity reflections for p - and s -polarised light, respectively, at various angles of incidence with respect to the total light intensity. Experimental results show that the changes for ellipsometric characteristics Ψ and Δ are the most strongest and they are very sensitive to environmental covering during monitoring in TIRE geometry.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11468-022-01594-y>.

Acknowledgements We would like to thank the support from EU Graphene Flagship Core 3 and Graphene NOWNANO CDT from the University of Manchester.

Author Contribution Vasyi Kravets and Alexander Grigorenko conceived the idea and developed the theory. Vasyi Kravets, Alexander Grigorenko and Fan Wu designed and performed the experimental sensor fabrication, ellipsometric measurements, materials and sensing characterizations and data analysis. Tongcheng Yu performed AFM measurements and theoretical simulations. All of the authors participated in manuscript preparation and revision processes.

Funding This work is supported by the Graphene Flagship programme, Core 3 (Grant No. 881603).

Availability of Data and Material All other data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Consent for Publication All authors agree to publish this paper.

Conflict of Interest The authors declare no competing interests.

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