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Optical Interference Substrates for Nanoparticles and Two-Dimensional Materials

Invited Review Article

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Abstract Interference substrates are useful in enhancing Raman and luminescence signals and in increasing the optical contrast of nanoparticles and atomically thin layers. Interference substrates played a crucial role in the discovery of the electric field effect on electronic conduction in graphene a few years ago. They are now used for a wide range of two-dimensional materials and recently for the heterostructures of atomically thin films. The same or similar substrates can be employed for the exploration of a large variety of nanoparticles. Although optical interference has been known to occur within the proximity of surfaces for more than one century, optical interference has been only gradually used over the last two decades to enhance the optical response of nanoparticles and layered materials. We review the different forms of interference substrates used over time. While multiple interference effects are frequently put forward to explain the enhancement in interference substrates, we show here that the formation of optical surface standing waves near strongly reflecting surfaces is the main cause of field enhancement. In addition, we demonstrate how a metal layer improves optical field enhancement.

Keywords Nanoparticles, Monolayer Materials, Optical Interference, Si/SiO_2 Substrate

1. Introduction

After the discovery of the exceptional electronic transport properties on flakes of graphene by Geim, Novoselov et al. at the University of Manchester (UK), there has been a tremendous surge of interest in the study of the electronic and optical properties of two-dimensional materials [1]. Making single atomic layers visible with conventional optical microscopy using oxidized silicon wafers was a crucial step in advancing the exploration of a few atomic layers of two-dimensional materials. The literature on the use of substrates to enhance the optical response of layered materials or nanoparticles is much dispersed, and we make here the first attempt to review the different contributions making use of planar substrates to enhance the optical response of nanoparticles and layered materials over the last two decades. We show that the formation of optical surface standing waves near strongly reflecting surfaces is the main cause of field enhancement.

2. Observing monolayer materials and nanoparticles

In principle, scanning probe microscopy can identify the presence of thin atomic sheets and determine their thickness and lateral dimension. However, scanning techniques are time consuming at the resolution required to discriminate between single or a few layers of a material restricting the scan area. Scanning electron microscopy, on the other hand, induces contaminants in the exposed region. The advantage of optical methods insofar as they are rapid and non-destructive makes them particularly suitable for large-area samples. Surface-enhanced Raman scattering (SERS) associated with island noble metal films or particles to enhance the optical response of molecular adsorbates and nanoparticles has been much explored over the past 40 years [2]. SERS relies on strong resonant coupling with nanostructured metal surfaces. The non-planar surface, the formation of hot spots due to complex geometries and its dependence on the chemical properties of the nanoparticles (NPs) limits its application, however.

3. Bi- and trilayer substrates

Using planar dielectric surfaces by making use of optical interference to enhance the optical response, simplifies the geometry and does not rely on resonant processes; therefore, the enhancement does not depend on the chemical properties of the atomic layers or NPs. The first substrate making use of optical interference to enhance the optical response was explored by Namanich et al. [3]. Nemanich used a trilayer structure to enhance the Raman signal from a Te layer through optical interference. The Te layer - 5 nm thick - was deposited on a SiO_2 layer on top of an Al substrate. The thickness of the SiO_2 layer was used to reduce the reflectance of the trilayer. It was argued that minimizing the reflectance increases the interaction with the Te layer and enhances the Raman signal. In order to obtain a low reflectivity, the top layer had to be sufficiently absorbing and thick. The trilayer structure was particularly useful in absorbing layers such as metals, and has been applied to study the phonon spectrum of amorphous nickel-Bohr layers [4]. The same trilayer structure was later adapted to the study of semiconductor clusters by using an absorbing amorphous carbon top layer to minimize the optical reflectivity at the excitation frequency [5]. This trilayer substrate was employed to study the vibrational properties of Bi clusters [6] as well as the vibrational spectrum of covalently adsorbed Al on Ge clusters in an ultra-high vacuum [7]. To better understand the enhancement, the electric field across a trilayer structure was calculated using the Fresnel reflection coefficients, including multiple reflection and interference in the trilayer. The calculations showed that the primary effect of the enhancement was due to the large electric field in the top layer caused by the constructive interference of the incoming wave and the wave reflected by the metal substrate. The incident and reflected wave in fact form a standing optical wave parallel to the surface. However, an absorbing top layer reduced the amplitude of the transmitted wave and reduced its constructive interference with the reflected wave. This meant that the interference substrate could be simplified through a bilayer consisting of a reflecting substrate and a SiO_2 layer. The absence of the absorbing top layer has the effect that more light is reflected by the substrate, increasing the interference with the incoming wave at the surface of the SiO_2 layer and leading to a larger enhancement. The maximum of the optical standing wave falls on the bilayer surface provided by the thickness of the SiO_2 layer when using normal incidence is $(2m+1)\lambda/4n$ (m=1,2,3 ...), where n is the index or refraction of the substrate and λ is the incident wavelength. For a highly reflecting metal surface, the maxima of the standing wave is close to four times the electric field intensity in the air [8] and about 20-30 times the intensity of the optical field on a reflecting metal surface. The standing wave has a field minimum at the metal surface, reducing the electric field intensity.

Bilayer substrates have been used in combination with Ag nanoparticles [9, 10] for SERS and to take Raman spectra from isolated single wall carbon nanotube bundles [11].

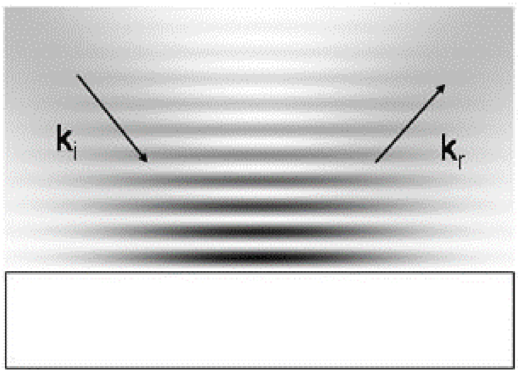

Figure 1. Time averaged electric field intensity near a highly reflecting substrate in the overlap zone of an incident and reflected Gaussian beam showing the formation of the optical surface standing wave. The optical surface standing wave has a field minimum at the surface for all absorbing surfaces.

4. Optical standing waves

Optical standing waves near surfaces were first observed by Wiener when recording interference fringes in photographic emulsions in front of a reflecting mirror [12]. The fringes of the standing waves oriented parallel to the surface are called 'surface standing waves' (SSWs). The existence of optical SSWs has been long overlooked since then, however. Harrick [13] studied standing waves in a transparent medium between two total reflecting interfaces. He was particularly interested in enhancing the field at the surface to increase the optical response of adsorbates. Harrick showed that the maximum electrical field amplitude at the air interface can also be two times the amplitude in air for a critical angle. The bilayer structure is less sensitive to the angle of incidence (10-20 deg.), however. The fringe spacing of SSWs increases monotonically with an increase in the angle of incidence. Surface standing waves were finally first used in x-ray optics to enhance the response of surface layers. Cowan et al. have demonstrated the existence of x-ray standing waves on a silicon surface and suggested their use in the study of surface atom location [14]. Surface structural analysis with x-ray standing waves has since become a widely used technique in studying surface adsorbates [15]. While SSWs have remained unexplored, the formation of standing waves within thin films has been explored in great detail. Holm et al. studied the photoluminescence signal of SiO_2 as a function of film thickness on a reflecting surface. This has been explained by the effect of multiple reflection and interference in thin films [16]. Similarly, when observing the Raman signal of nitrogen and oxygen layers on a silver substrate at low temperature, oscillations of the Raman signal have been observed as a function of film thickness [17]. The oscillations in the Raman intensity have been explained by multiple beam interferences in thin films. However, the amplitude of the reflected wave on transparent layers is small and, therefore, multiple interference effects are less important. The dominant effect is the formation of optical standing waves at the reflecting surface, which modulates the optical field parallel to the surface. Fromherz studied the photo-luminescence of dyes on silicon as a function of SiO_2 thickness motivated by previous work considering fluorescent molecules in front of a reflecting surface [18]. The modulation of the excitation and emission of dye molecules has been used to measure the distance between a stained cell membrane and the SiO_2 surface with a precision of 1.1 nm in the axial direction [19, 20]. Swan et al. showed that this sensitivity as to the thickness of the dielectric layer, can be increased by recording the entire emission spectrum using a considerably thicker SiO_2 layer (10 wavelength) to increase self-interference. This leads to interference fringes in the emission spectrum, enabling an increase in axial resolution. The separation between fluorophores attached to the top or bottom layers in lipid bilayer films could be determined with a precision of 0.3 nm in vertical direction [21].

Interference substrates have also been used in combination with scanning optical fibre probes in collection mode. The large field at the surface implies larger scattering by the nanoparticles on its surface. The larger local optical field can be recorded by an optical fibre probe. Metal island films have been recorded on interference substrates and an optical fibre probe in collection mode at a resolution as small as 40 nm [22, 23, 24].

5. Making atomic layers visible

Geim and Novoselov used the bilayer Si/SiO_2 substrate to increase the optical contrast of thin flakes of graphite obtained by adhesive tapes from highly-oriented pyrolytic graphite (HOPG) [1]. It was demonstrated that the contrast from thin layers of graphite is sufficiently large on a Si/SiO_2 substrate to make a single layer of graphene visible using conventional optical microscopes. This allowed the screening of graphene flakes and simplified the deposition of electrodes for electronic transport measurements. Nanostructures have been imaged using cross-polarized light with a Si/SiO_2 substrate [25]. The discovered unique electronic properties of graphene, high charge carrier mobility and strong electric field effect had a huge impact in the consideration of graphene for future high speed electronics. Blake et al. systematically explored the optical contrast of graphene on the Si/SiO_2 interference substrates as a function of SiO_2 thickness and wavelength, showing that the contrast is higher in the 400-500 nm range [26]. Roddaro et al. studied the influence of the thickness of ultrathin graphite layers and a SiO_2 layer on optical reflectance and showed that the contrast can be improved by monochromatic illumination [27]. Jung et al. [28] used a silicon nitride layer instead of a SiO_2 layer to increase the optical contrast. Silicon nitride has a high refractive index (2.02 @ 587 nm), which increases the optical contrast for ultrathin layers. Shen et al. [29] quantified the optical contrast as a function of wavelength and the number of graphene layers and was able to deduce the complex index refraction of graphene ($n_{graphene} = 2.0 + 1.1$ i, $n_{graphite} = 2.6 + 1.3$ i). With increasing thicknesses, the graphene layer gets first darker and is reflective when thicker than 10 atomic layers. It has been shown that Raman scattering can be used to determine the thickness of a few atomic layers by taking into account interference effects [30, 31].

This enormous success in the discovery of the electronic properties of graphene had the result that a large number of layered compounds are now studied using interference substrates in exploring electric field-induced transport properties. Eklund et al. studied the superconductivity of atomically thin flakes of $NbSe_2$ [32]. Heinz et al. investigated the vibrational properties of single layer and a few layer MoS_2 [33, 34], while Balandin et al. studied electron transport in $TiTe_2$ [35-39]. Recently, the reflectance and morphology of silver island films on a bilayer substrate has been investigated [40]. Yoon et al. [38] have shown how the thickness of the oxide layer influences the relative intensity of the Raman D, G and two-dimensional band in graphene. Gaskill et al. [38] showed that the optical reflection of graphene layers can also be observed on transparent substrates, although with a considerably smaller contrast (7.1%). Ling et al. [42] and Jung et al. [43] compared the Raman signal of a variety of molecules deposited on interference substrates both with and without a graphene layer and found that the Raman signal on graphene is enhanced. However, a detailed analysis of rhodamine 6G dye molecules on graphene showed no enhancement, and the previously reported enhancement has been attributed to the higher molecular adsorption rate on graphene as compared to that on SiO_2 [44, 45].

The development of interference substrates was first initiated by the need to enhance the Raman signal of ultrathin layers and molecular adsorbents, resulting in the use of first trilayer and, later on, bilayer substrates. Interest in understanding the photoluminescence of thin films on a reflecting surface led to the use of the same interference substrate, showing high accuracy in determining distances perpendicular to the surface. This high sensitivity to molecular layers was finally used by Geim and Novoselov to make the monolayer visible in optical reflection microscopy.

6. Increasing the optical field at the substrate surface

We have seen that optical signals are increased due to the higher optical field at the interference substrate. In the following, we show how the optical field can be increased using a metal layer. Figure 2 compares the electric field intensity across the interference substrate when using Al or Si as a reflecting substrate (wavelength 500 nm).

The higher reflectivity of the Al leads to higher field intensity at the surface of the interference substrate, and the reflectivity is close to the maximum for two beam interference - four times the field intensity in vacuum. This means that Raman and photoluminescence signals are larger on an interference substrate with an Al substrate. The formation of standing waves near a reflecting surface is similar to the field distribution in optical cavities, and the combination of a highly reflecting surface with a dielectric layer can be viewed as a half cavity. Fig. 3 compares the relative and absolute contrast for the two types of substrates. Relative contrast is the difference in the amplitude of the reflected light with and without one graphene layer divided by the amplitude of the reflected light without any graphene layer, while absolute contrast is simply the difference of amplitude of the reflected light with and without one graphene layer. While the relative contrast is somewhat smaller when using an Al/SiO_2 substrate, the absolute field intensity is larger than for the Si/SiO_2 substrate. This means that with the use of an aluminium layer the substrate is brighter in the optical microscope.

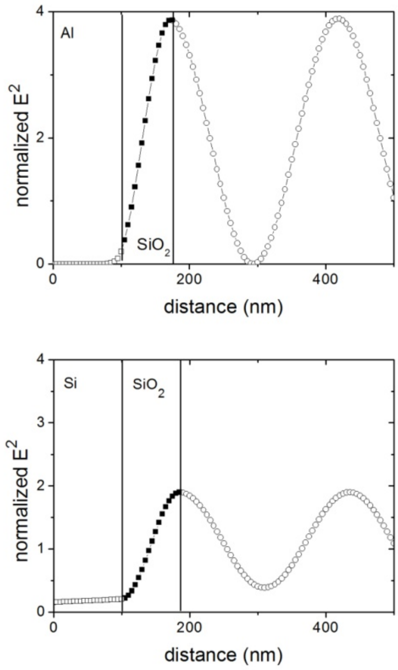

Figure 2. Time averaged electric field intensity near a highly reflecting substrate in the overlap zone of an incident and reflected showing the formation of the optical surface standing wave. The optical surface standing wave has a field minimum at the surface for all absorbing surfaces

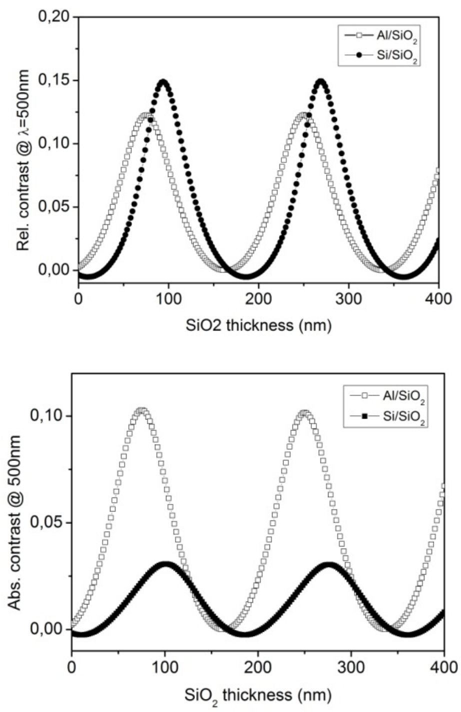

Figure 3. Relative (top figure) and absolute (bottom figure) contrast for the two types of substrates using an incident beam with a wavelength of 500 nm.

Although the optimal thickness is calculated for normal incidence, high numerical aperture objectives imply that a portion of the light comes in at an angle. This leads to larger fringe spacing's of the optical standing wave, which needs to be taken into account when optimizing the thickness of the SiO_2 layer. A numerical aperture of 0.95 results in a maximum angle of incidence of 40.5 deg. Fig. 4 compares the relative and absolute contrast of the two types of substrates as a function of the thickness of the Si/SiO_2 layer when taking an angle of incidence of 40.5 deg. The contrast increases by 30% at 40.5 degrees when using an Al layer. The optimal thickness of the Si/SiO_2 layer is, as a result, larger with an increasing angle of incidence. A large numerical aperture therefore leads to a broadening of the standing wave and a larger optimal thickness of the SiO_2 layer. For thicker layers, the amount of light reflected and transmitted changes. This influences the amplitude of the surface standing wave at the surface of the interference substrate. Fig. 5 shows the calculated electric field intensity across the interference substrates when increasing the number of graphene layers. The maxima of the surface standing wave decreases continuously with an increase in the number of graphene layers, reducing the field enhancement effect. For five graphene layers, the field intensity decreases by 24%. The intensity profile of the electric field also shows that the position of the maximum of the surface standing wave shifts and the field at the interface gets smaller than the first maxima near the substrate when the thickness of the graphene layer is increased.

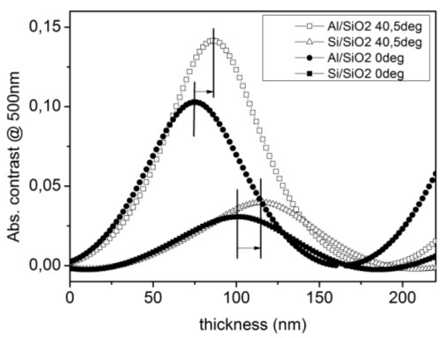

Figure 4. Absolute contrast for Al/SiO_2 and Si/SiO_2 substrates at normal incidence and an angle of incidence of 40.5 deg. using an incident beam with a wavelength of 500 nm.

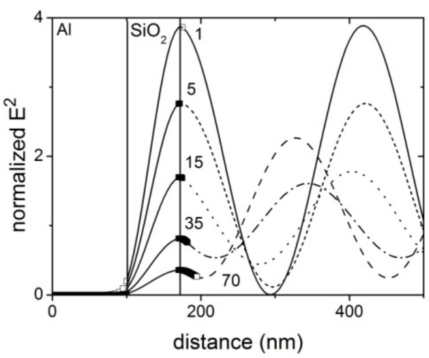

Figure 5. Electric field intensity profile as a function of the number of graphene layers. The standing wave is strongly influenced by the number of graphene layers. The wavelength of the incident beam is 500 nm.

7. Conclusion

We reviewed the use of optical interference substrates to enhance the optical response of nanoparticles and layered materials. Considerable time has passed since the first observation of optical surface standing waves by Wiener and the use of interference substrates to enhance Raman and photoluminescence signals. Fundamental interest in optical fields and optical signals near surfaces was first used to design substrates to take advantage of optical standing waves to enhance luminescence and Raman signals, as well as to measure the thickness of lipid bilayer membranes with sub-nanometre resolutions. Finally, interference substrates were used to make atomically thin layers visible for the exploration of layered and two-dimensional materials. While the advantages of interference substrates are often attributed to multiple beam interferences, a closer examination shows that it is the formation of optical standing waves near strongly reflecting surfaces which enhances the interaction of atomically thin layers and NPs in interacting with the incident beam. We have compared two interference substrates with a metallic and semiconducting absorbing substrate. We have shown that the electrical field intensity is four times larger but that the optical contrast is slightly lower for the metal substrate. The SiO_2 layer is 10-20% thicker for the metallic substrate, and a large numerical aperture improves contrast and broadens the surface standing wave maxima at the surface of the interference substrate.

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