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ANTENNA RESONATOR MODEL OF SERS AND STUDY OF THIN SOLID FILMS AND ADSORBED MOLECULES ON THE SURFACE BY SERS

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ABSTRACT

In this thesis, some new results on the study of mechanism and application in surface enhanced Raman scattering (SERS) will be presented.

A new SERS substrate made by a chemically deposited silver mirror has been described. It has a very large enhancement factor and a rather homogeneous surface roughness, good time stability and it is easy to prepare. Now the silver mirror substrate and its method of chemical deposition have become common in SERS technique.

Our systematic experimental investigation of the dependence of enhancement on silver surface roughness shows that the enhancement is extremely sensitive on the macroscopic surface roughness, but not on the microscopic one. A maximum enhancement has been obtained for a surface roughness of 100nm for silver in the excitation range 514.5-602nm, and of 50nm for copper in the excitation range 602-664nm.

We have proposed an antenna resonator model to explain our SERS experimental data. In this model, the particle or the protrusion of the SERS substrate is considered as an electromagnetic antenna resonator. Then the enhancement factor and its dependence on experimental parameters (e.g. the dependence excitation wavelengths, surface roughness, etc.) could be calculated for any substrate from its dielectric constant. The comparison between the calculation and the experimental data shows that this model can well explain the dependence of the enhancement on the surface roughness of Ag and Cu, the small enhancement from a roughened Cu surface at 488nm excitation as well as from a roughened Zn surface at red laser excitation. The missing enhancement from the roughened surface of Al metal produced by lithography or a polishing method at 488nm excitation and could be just as well explained as the large enhancement of a Ag, Cu and Au surface at 1.06μm wavelength excitation.

We have also used the SERS technique to study thin solid films and some molecules adsorbed on SERS active surfaces:

Clear SERS bands from extrathin α-Si films have been observed with the silver overlayer method (α-Si film on the top) and a natural oxidized layer of Si with a thickness of 0.7-0.8nm was determined. Using the silver top layer (silver on the top), the feature in the Raman spectrum disorder-induced phonon density of states (DOS) of epitaxially stabilized $FeSi_2$ films have been observed by SERS. The coherently strained film showed a Raman band with a lower energy than the relaxed one that can be well explained by the distortion arising from the misfit of -0.5%.

The SERS study on C_{60} proofs a physiadsorption of C_{60} molecules on the silver surface in our case. Using SERS technique, we have observed about ten new Raman bands from C_{70} which were not previously reported. By the study of time evolution of the SER spectrum taken with a micro-Raman under a high laser power density illumination (about $5x10^4$ W/cm^2) in air, new bands, attributed to some intermediate products (probably some organic compounds such as ophthalmic anhydride from photochemical reaction of C_{70}) have been observed and discussed.

The experimental results of the study of surfactants of TX-100 and CPyB adsorbed on a silver surface in water solution has clearly given their adsorption configuration on silver: the phenol ring of TX-100 and the pyridinium cycle lies standing up on the silver surface, and the EO chain of TX-100 stretches into the aqueous phase, but the alkane chain stretches tortuously on the silver surface with some parts of the chain adsorbed on the surface. We observed a phase transition of adsorbed PNBA molecules on the copper surface by changing the concentration of KCl, C_{KCl}, in the solution. When C_{KCl} is lower than a critical value, PNBA is adsorbed on the copper surface through the NO^-_2 group and then it is adsorbed through the carboxylate group. The surface enhanced resonance Raman scattering (SERRS) detection limit of the full spot for Co(II)TsPc is reached at about 10pg by using a silver mirror substrate. From the analysis of those Raman spectra we concluded that the molecules of Co(II)TsPc adsorb standing up on the metal surface through the SO^-_3 group.