Quantum Electronics **40** (4) 346 – 348 (2010)

NANOSTRUCTURES

PACS numbers: 68.08.–p; 42.62.–b; 81.07.–b; 42.65.Dr
DOI: 10.1070/QE2010v040n04ABEH014259

Generation of surface nanostructures on nickel by liquid-phase laser ablation and their surface-enhanced Raman scattering activity

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Abstract. **Surface nanostructuring of nickel by ablation with 350-ps Nd : YAG laser pulses in ethanol has been studied experimentally. The morphology of the nanostructured surface has been examined using a field emission scanning electron microscope. The average lateral size of the surface nanostructures is 30 – 50 nm. The nanostructured surface has been coated with gold using a chemical deposition procedure. The gold-coated substrate has shown surface-enhanced Raman scattering with an enhancement factor of 10^8. Potential applications of such nanostructured targets are discussed.**

Keywords: *laser ablation, surface nanostructures, surface-enhanced Raman scattering.*

1. Introduction

Surface nanostructures produced by laser ablation of metals in liquids have attracted researchers' attention relatively recently. Their formation is accompanied by changes in the absorption spectrum of the target – additional absorption bands emerge near the plasmon resonances in the metal nanostructures – and changes in surface wettability. Moreover, the nanostructured metals exhibit surface-enhanced Raman scattering (SERS) from adsorbed molecules.

Self-organising nanostructures of this kind were first observed on silver [1] and then on gold [2, 3], after ablation with picosecond laser pulses in water. In addition, such surfaces were found to be SERS-active, with enhancement factors of 10^5 and 10^4, respectively. The SERS effect was shown to arise from local enhancement of the electromagnetic field of the incident light at nanospikes. Later, surface nanostructures were also produced on tantalum by ablation with pico- and femtosecond laser pulses in water. Their average lateral size was shown to decrease with decreasing pulse energy density and duration [4]. Stratakis et al. [5, 6] obtained surface nanostructures on aluminium by ablation with femtosecond laser pulses in air and liquids. It seems likely that the formation of such self-organising structures is due to the development of instability at the interface between the melt and the vapour of the liquid adjoining the melt.

The interest in extending the class of materials on which such nanostructures can be produced is motivated by the fact that, at the present stage, this process defies theoretical description because jointly solving the heat and Navier – Stokes equations is a challenging problem. In this context, accumulation of experimental data on the properties of such nanostructures would be expected to provide greater insight into the mechanism of their formation and expand the application field of nanostructured substrates. In particular, nanostructures on ferromagnetic materials are potentially attractive as high-density magnetic recording media. Nanostructured surfaces are SERS-active, which is of particular interest in designing sensors for environmental monitoring applications. The SERS effect is typical of noble metal (gold and silver) nanostructures. Bulk substrates from these materials are however too expensive. A more economical approach is to deposit gold or silver on nanostructured surfaces of less expensive metals, e.g. nickel. The objective of this work was to produce surface nanostructures on nickel and to assess the SERS efficiency of such nanostructures coated with gold.

2. Experimental

As targets we used 100-μm-thick nickel plates. Prior to irradiation, the targets were abrasively ground or polished to the desired roughness value (about 50 nm) and placed on the bottom of a glass cuvette, which was then filled with ethanol.

Surface nanostructures on nickel were produced using 1.06-μm Nd : YAG laser pulses (pulse duration, 350 ps; repetition rate, 300 Hz). The cuvette was mounted on a computer-controlled stage which ensured a constant translation velocity relative to the laser beam. The beam was focused onto the target through a liquid layer several millimetres in thickness. The beam spot area on the target was determined from the dimensions of the modified zone.

The surface morphology of the irradiated targets was visualised using field emission scanning electron microscopy (FESEM). Gold was deposited on the nanostructured nickel surface by a chemical procedure using a standard gold electrolyte solution, as described elsewhere [7]. Raman spectra of *trans*-1,2-bis(4-pyridyl)ethylene (BPE) and Meth-

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Received 1 December 2009
Kvantovaya Elektronika **40** (4) 346 – 348 (2010)
Translated by O.M. Tsarev

ylene Blue (MB) molecules were excited using the 632.8-nm He–Ne laser line. The exposure time was 1 min. The beam was focused onto the sample surface by a $100^{\times}$ immersion objective. Specific details of SERS measurements can be found in Lau Truong et al. [2, 3].

3. Results and discussion

Figure 1 illustrates the surface morphology of nickel before and after ablation with Nd : YAG pulses under an ethanol layer. As seen, laser ablation produced nanostructures on the initially smooth surface. Their average lateral size is 30–50 nm. SERS data for nanostructured nickel are not available in the literature. Surface nanostructures produced on nickel can be used as templates for the growth of nanoislands of other metals, e. g. gold.

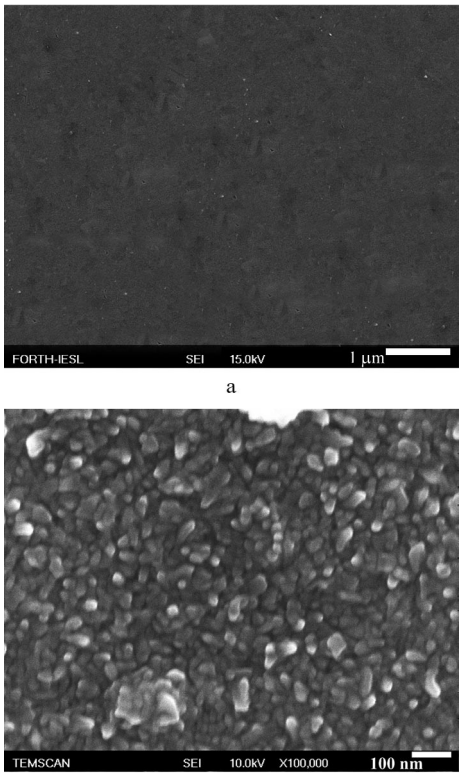

Figure 1. FESEM images of nickel (a) before and (b) after ablation with 350-ps Nd : YAG pulses in ethanol.

Figure 2 shows the nickel surface after gold deposition from a standard electrolyte solution. The gold deposition process was accompanied by gradual nickel dissolution in the form of ions. The resultant nanostructures had the form of polyhedra. Gold was also deposited on the unexposed part of the target, where gold crystals were considerably larger, as seen at the periphery of Fig. 2.

The gold-coated nickel nanostructures were characterised by SERS measurements. Figure 3 shows Raman spectra of BPE molecules. When there was no target, no Raman signal from BPE was detected, even at a BPE concentration of 0.1 M, and the spectrum showed only a peak around 1450 cm^{-1}, due to ethanol. The presence of gold-coated nanostructured nickel led to Raman signal enhancement, even when the

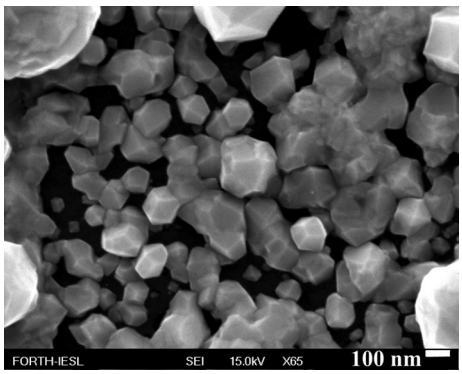

Figure 2. Morphology of a nanostructured nickel surface after chemical deposition of gold.

solution concentration was four orders of magnitude lower (10^{-5} M). In Fig. 3, the two characteristic peaks of BPE, at 1607 and 1633 cm^{-1}, are quite prominent. Thus, gold-coated surface nanostructures on nickel markedly enhance the Raman response of the test compound.

Let us assess this enhancement. The electromagnetic field is enhanced near surface nanostructures over a distance of the same order as their size. Therefore, to estimate the enhancement factor, the number of molecules in a 100-nm-long cylinder with a base area of 1 μm^2, equal to the laser beam spot area on the target, at a solution concentration of 10^{-5} M should be determined. We find that the number of molecules is 100. When there is no target and the solution concentration is 0.1 M, the beam 'volume' (10 μm^3, where 10 μm is the effective waist length) contains 10^8 molecules. The SERS peak of BPE is observed at a Raman shift of 1605 cm^{-1}. The Raman signal is 1700 cps (counts per second) in the presence of a gold-coated nanostructured nickel target and 10 cps when there is no substrate in the BPE solution. Therefore, the signal enhancement factor for the gold-coated nanostructured nickel surface is 10^8, corresponding to SERS.

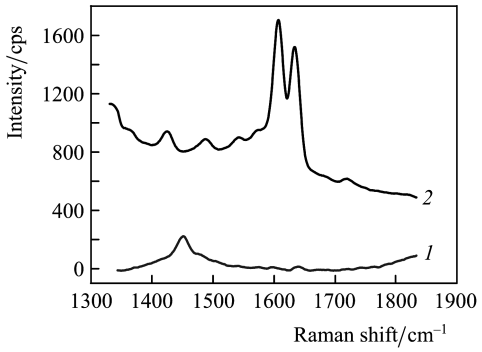

Figure 3. Raman spectra of BPE molecules: (*1*) 0.1-M BPE solution in ethanol; (*2*) 10^{-5}-M BPE solution in ethanol in contact with a nanostructured zone on a gold-coated nickel target.

Note that the Raman signal from smooth gold-coated areas on the nickel target does not exceed the background level, which implies that there is no specific adsorption of BPE molecules on gold.

We also obtained the Raman spectrum of MB molecules adsorbed on a gold-coated nanostructured nickel surface.

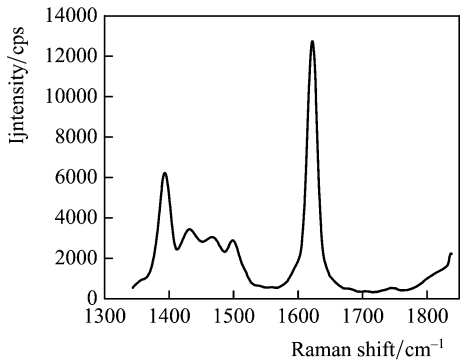

Figure 4. Raman spectrum of Methylene Blue molecules adsorbed on a gold-coated nanostructured nickel surface.

Since MB strongly absorbs the He–Ne laser output, in studies of SERS from MB molecules the target was immersed in an aqueous MB solution for several minutes, then withdrawn from the solution and washed with deionised water. The residual liquid was removed by drying. It is commonly thought that under such conditions the MB surface coverage is one monolayer. The Raman spectrum of MB molecules is presented in Fig. 4.

MB has a rather large Raman cross section at 632.8 nm because of the resonance enhancement, which contributes to the Raman signal. In this study, the scattering signal intensity for MB on a gold-coated nanostructured nickel surface is 12 700 cps, the signal being generated by an MB monolayer.

As mentioned above, surface nanostructures produced on gold by ablation with picosecond laser pulses in water exhibit SERS with an enhancement factor of 10^4 [2], whereas the gold-coated nanostructured nickel surface ensures a Raman signal enhancement of 10^8. The reason for this is that the surface nanostructures in question differ in morphology. As seen in Fig. 2, the gold-coated nickel nanostructures have the form of polyhedra with rounded corners. Their radius of curvature is much smaller than the radius of the surface nanostructures on gold ($\sim$100 nm), so the field near the former nanostructures is considerably stronger. Thus, the signal from a gold-coated nanostructured nickel surface is several orders of magnitude stronger than that from a nanostructured gold target.

The present data demonstrates that the Raman signal enhancement on gold-coated nanostructured nickel surfaces reaches 10^8, which suggests that such substrates are candidate sensors for environmental monitoring applications. Such sensors would be much less expensive than all-gold sensors because the SERS-active metal, gold, is deposited as a thin layer. Another potential application of nanostrutured nickel surfaces is information storage. The surface density of nanostructures as estimated from Fig. 1b is 4×10^{10} cm^{-2}. If one bit of information could be written on each nanostructure, the recording density would be 10 Gb cm^{-2}, which far exceeds that in all existing storage media.

4. Conclusions

Ablation of nickel targets with 350-ps laser pulses in ethanol produces surface nanostructures with a typical lateral size from 30 to 50 nm. Gold deposition on such nanostructures ensures SERS from adsorbed BPE and MB molecules, with an estimated enhancement factor of 10^8. Such substrates are of interest as potential sensors for environmental monitoring applications and also for the development of information storage media.

Acknowledgements. This work was supported in part by the Russian Foundation for Basic Research (Grant Nos 07-02-00757 and 08-07-91950) and the RF President's Grants Council for Support to the Leading Scientific Schools (Grant No. NSh-8108.2006.2; coordinator, F.V. Bunkin).

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