

2. X. Wei, S.-C. Hong, X. Zhuang, T. Goto, and Y.R. Shen, *Phys. Rev. E* **62**, 5160 (2000).
3. X. Wei, and Y.R. Shen, to be published.
4. S. Woutersen, U. Emmerichs, and H.J. Bakker, *Science* **278**, 658 (1997)
5. Q. Du, R. Superfine, E. Freysz, and Y.R. Shen, *Phys. Rev. Lett.* **70**, 2313 (1993).

QThF2

10:30 am

Experimental observation of percolation-enhanced nonlinear light scattering from semicontinuous metal films

M. Breit, G. von Plessen and J. Feldmann, *Photonics and Optoelectronics Group, Physics Department and CeNS, University of Munich, D-80799 München, Germany*

S. Gréillon, J.C. Rivoal and P. Gadenne,[†] *Lab. Optique Physique, ESPCI, CNRS-UPR5 and Université P. et M. Curie, 75231 Paris, France;* [†]L.M.O.V., *Université de Versailles Saint Quentin, CNRS UMR 8634, F-78035 Versailles, France*

V.A. Podolskiy, Andrey K. Sarychev and Vladimir M. Shalaev, *Department of Physics, New Mexico State University, Las Cruces, NM 88003, USA;* *Email: Michael.Breit@physik.uni-muenchen.de*

In random metal-dielectric films where the metal coverage of the dielectric substrate is close to the percolation threshold, disorder-induced localization of plasmons occurs, resulting in huge fluctuations of local fields.¹ One of the most interesting theoretical predictions for such percolation films is that nonlinear light scattering at the n th frequency harmonic $n\omega$ of an incident beam can be significantly enhanced and is characterized by a broad, nearly isotropic angular distribution.² According to theory, this effect, which was denoted in² as percolation-enhanced nonlinear scattering (PENS), is caused by the huge local-field fluctuations associated with the localized plasmons. Here we experimentally verify the existence of the PENS effect by measurements of the second harmonic generation from semicontinuous and continuous gold films.

Samples of percolation metal films were prepared by controlled evaporation of gold on a glass substrate.⁴ For comparison, we also deposited smooth continuous gold films. The measure-

ments were done with a pulsed light beam at $\lambda = 800$ nm (corresponding to ω) with pulse duration of 150 fs, which was incident at -45° with respect to the film normal, as shown in Fig. 1, and was either s or p polarized. Linear and nonlinear light scattering from the percolation metal film results in coherent beams in specularly reflected and transmitted directions and also in diffuse light (Fig. 1). The scattered light was detected using photon-counting. For angular dependence measurements, the photomultiplier was moved around the sample. Results of our experimental studies obtained on percolation films are shown in Fig. 2. SHG signals were detected at 400 nm (corresponding to 2ω) in the specularly reflected and transmitted directions, 45° and 135° , respectively. In addition to these coherent SHG components, a strong diffuse-like signal, characterized by a broad angle distribution, was measured, as shown in Fig. 2. The total (integrated) intensity of this diffuse SHG component exceeds the intensity of the coherent component reflected in the specular direction by factor of 350, for p-polarized incident light, and by 10^3 , for s-polarized light. It is important to note that the highly diffuse character of this SHG component is a signature of the predicted PENS effect.² For comparison, linear scattering of incident light at 800 nm was also measured on the same percolation film (solid line in Fig. 2). In contrast to the SHG signal, the angle-integrated diffuse component is smaller than the components of the linear signal in the reflected and transmitted directions by a factor of 240. This observation confirms the theoretical expectation² that linear scattering from percolation films is much less diffuse than PENS.

For comparison measurements of light scattering were also performed on continuous (i.e., smooth) gold films. When compared to the SHG intensity reflected from such a continuous gold film, the total diffuse SHG from a percolation gold film was greater by a factor of 40, for p-polarized incident beam, and by roughly 10^3 , for s-polarization. This enhancement is in excellent agreement with the result of a model calculation based on the approach described in Ref. [2]. The enhancement is a consequence of the huge local-

field enhancement provided by plasmon localization in percolation films.

References

1. V.M. Shalaev, A.K. Sarychev, *Phys. Rev. B* **57**, 13265 (1998); S. Gréillon, et al., *Phys. Rev. Lett.* **82**, 4520 (1999); A.K. Sarychev, et al., *Phys. Rev. B* **60**, 16389 (1999); V.M. Shalaev, *Nonlinear Optics Of Random Media: Fractal Composites and Metal-Dielectric Films* (Springer, Heidelberg, 2000).
2. A.K. Sarychev, et al., *Phys. Rev. E* **59**, 7239 (1999); A.K. Sarychev and V.M. Shalaev, *Phys. Rep.* **335**, 275 (2000).
3. M. Breit, et al., submitted to *Phys. Rev. Lett.*
4. Y. Yagil, et al., *Phys. Rev. B* **46**, 2503 (1992); P. Gadenne, et al., *J. Appl. Phys.* **66**, 3019 (1989).

QThF3

10:45 am

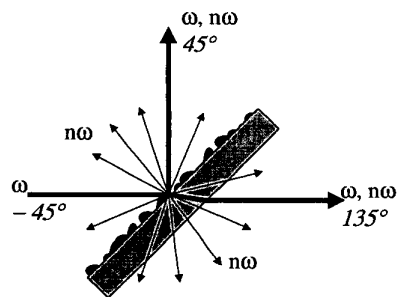
Sum Frequency Spectroscopy Studies of Adsorption of Additives on Metal/Electrolyte Interfaces

C.S.C. Yang, L.J. Richter, *Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA; Email: Clayton.yang@nist.gov*

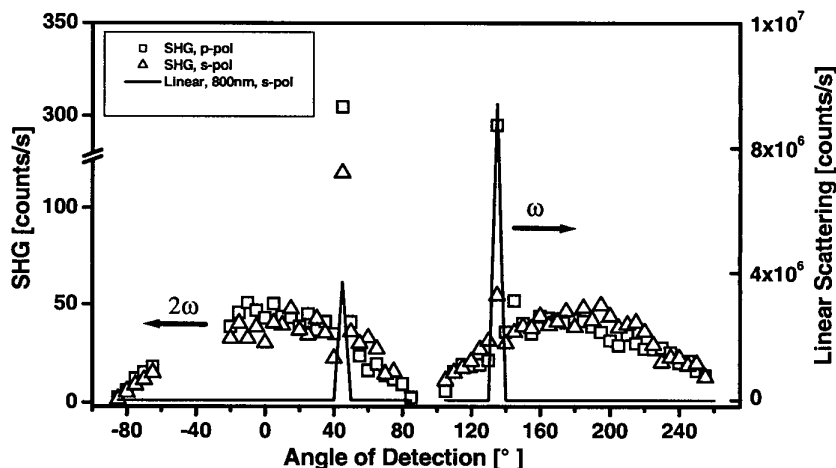
K.A. Briggman, J.C. Stephenson, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*

T.P. Moffat, G.R. Stafford, *Metallurgy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*

Copper is rapidly being introduced into chip interconnection technology as a replacement for aluminum. Copper electrodeposition has an advantage over aluminum physical deposition in its ability to allow superconformal deposition and 'superfilling' of trenches and vias in the Damascene process when additives (inhibitors, accelerators) are present in the plating bath.¹ An additive formulation that has been shown to exhibit superfill contains NaCl, 3-mercaptop-1 propanesul-



QThF2 Fig. 1. Linear reflection and transmission at frequency ω , and diffuse-like PENS (at frequency $n\omega$) from a percolation metal-dielectric film.

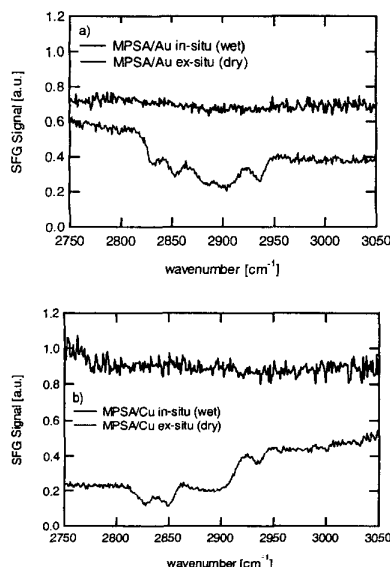


QThF2 Fig. 2. Angular distributions of reflected/transmitted light and of SHG from percolation gold-glass film; the polarizations of the incident light are indicated. The gap in the SHG data near -45° is due to the excitation set-up.

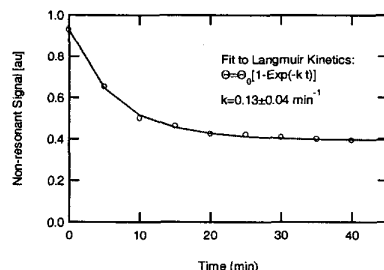
fonate (MPSA), and polyethylene glycol (PEG).² However, although it is recognized that copper inhibition is essential to achieve superfill, the overall mechanism and role of each additive in achieving superfill is still under debate due to the lack of understanding these processes on the molecular level.

It has been suggested that the competition between inhibition provided by the Cl-PEG/Cu²⁺/Cu⁺/Cu interaction and the catalytic effects of Cl-MPSA/Cu²⁺/Cu⁺/Cu interaction leads to an irreversible change in the reaction dynamics at the metal/electrolyte interfacial region.² As a first step toward accurately characterizing the structure of the surface species and determining the mechanism of the reaction in the metal/electrolyte interfacial region, we have made both *in situ* and *ex situ* measurements of vibrational spectra of adsorbed MPSA at metal/electrolyte interfaces using the nonlinear optical technique of vibrationally resonant sum frequency generation (VR-SFG). VR-SFG is uniquely interface specific and has been applied broadly to the *in situ* studies of solid/liquid interfaces.^{3,4}

Detailed analysis of vibrational spectra can provide information on the local order of the surface species and their orientation. We measured *ex situ* VR-SFG spectra of MPSA self-assembled from a perchloric acid solution on both gold and copper substrates (Figure 1). Five resonant features between 2800 and 2950 cm⁻¹ can be attributed to the CH₂ group of MPSA. Similar spectra recorded for alkane-thiol [CH₃(CH₂)_nSH] self-assembled monolayers, has shown the CH₂ groups do not generate significant VR-SFG signal when the molecule is in an all trans conformation.⁵ Therefore the observation of CH₂ modes in the *ex situ* spectra tells us the molecule on the dry metal surface must contain gauche defects. Figure 1 also shows the *in situ* VR-SFG spectra on both metal surfaces after 45 minutes of exposure to MPSA/perchloric acid solution. The *in situ* spectra fail to show the CH₂ features although an ob-



QThF3 Fig. 1. VR-SFG spectra of the (a) Au surface and (b) Cu surface after 45 min. exposure to MPSA/perchloric acid solution, and the same surface after drying.



QThF3 Fig. 2. Time evolution of the non-resonant background from the Au surface in contact with 20 mmol/L MPSA in 10 mmol/L perchloric acid solution.

served decrease in the non-resonant background indicates the adsorption of sulfur, presumably MPSA, onto the metal substrates as shown in Figure 2. Apparently the behavior of MPSA on copper is similar to that on gold: full hydration of the charged sulfonate (SO₃⁻) end group of MPSA results in an all-trans conformation of the molecules, and thus low SFG signal.

Unlike the CH₂ modes studied above, the stretching mode of the sulfonate end group (SO₃⁻) at 1070 cm⁻¹ is SFG active for all conformations of the MPSA molecule. Extensions of this *in situ* study on metal electrode surface under potential control in this frequency region will be presented.

References

1. P.C. Andricacos, C. Uozoh, J.O. Dukovic, J. Horkans, H. Deligianni, "Damascene copper electroplating for chip interconnections," IBM J. Res. Develop. 42, 567-574 (1998).
2. T.P. Moffat, J.E. Bonevich, W.H. Huber, A. Stanishevsky, D.R. Kelley, G.R. Stafford, and D. Josell, "Superconformal Electrodeposition of Copper in 500-90 nm Features," J. Electrochem. Soc., In Press.
3. C.D. Bain, "Sum-Frequency Vibrational Spectroscopy of the Solid/Liquid Interface," J. Chem. Soc. Faraday Trans. 91, 1281-1296 (1995).
4. L.J. Richter, T.P. Petrali-Mallow, J.C. Stephenson, "Vibrationally resolved sum-frequency generation with broad-bandwidth infrared pulses," Optics Lett. 23, 1594-1596 (1998).
5. M. Himmelhaus, F. Eisert, M. Buck, M. Grunze, "Self-Assembly of n-Alkanethiol Monolayers. A Study by IR-Visible Sum Frequency Spectroscopy (SFG)," J. Phys. Chem. B 104, 576-584 (2000).

QThF4

11:00 am

Molecular order at polymer interfaces measured by broad-bandwidth vibrationally-resolved sum frequency generation spectroscopy

P.T. Wilson, K.A. Briggman, J.C. Stephenson, W.E. Wallace and L.J. Richter, *National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899-8372*; Email: philip.wilson@nist.gov

1. Introduction

Measurement of the structure of polymer/dielectric interfaces is crucial to an understanding of

adhesion between such materials. Vibrationally-resolved sum frequency generation (VR-SFG) spectroscopy is a non-invasive, interface specific and chemically sensitive probe of the buried interfaces of transparent media.¹ The use of broad bandwidth femtosecond pulses enables the parallel acquisition of spectra across an entire resonant spectral range without laborious laser tuning.² The coherence of SFG allows the measurement of the phase of the VR-SFG signal relative to a non-resonant reference, which reveals the absolute orientation of the resonant molecular species.³

2. Experiment

A polystyrene/dielectric/Au microcavity was fabricated with a ~130 nm polystyrene (PS) thin film and varying thicknesses of a commercially available spin-on hydrogen silsesquioxane dielectric.⁴ The thickness of the dielectric determines the phase between the SFG generated in reflection and SFG generated in transmission and reflected from the Au substrate. Appropriate choice of the dielectric thickness can enhance the signal from either PS interface through constructive interference and null the signal from the other interface. VR-SFG spectra of the C-H stretch modes of the phenyl groups of polystyrene have been measured for these structures.

As shown in Figure 1a, a 207 nm dielectric layer selectively enhances the signal from the polystyrene/air interface which attenuates upon surface degradation by ozone exposure. As shown in Figure 1b, a 340 nm layer reveals the buried polystyrene/dielectric interface, which remains robust upon ozone exposure. Fits of the spectra of these two interfaces reveal resonances of the ν_2 and ν_{7a} modes of similar amplitudes, but opposite sign relative to the non-resonant spectral envelope from the Au substrate demonstrating that the interfacial phenyl groups are oppositely oriented away from the bulk of the film.

Further investigation and comparison with previous results demonstrates that the molecular orientation and degree of macroscopic ordering varies with the underlying dielectric.⁵

1. C.D. Bain, "Sum-frequency vibrational spectroscopy of the solid/liquid interface," Chem. Soc. Faraday Trans. 91, 1281-1296 (1995).
2. L.J. Richter, T.P. Petrali-Mallow, J.C. Stephenson, "Vibrationally resolved sum-frequency generation with broad-bandwidth infrared pulses" Opt Lett 23, 1594-1596 (1998).
3. R. Superfine, J.Y. Huang, Y.R. Shen, "Phase measurement for surface infrared visible sum-frequency generation," Opt Lett 15, 1276-1278 (1990).
4. FOx-14 Flowable Oxide, Dow Corning, We identify certain commercial equipment, instruments, or materials in this article to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
5. K.S. Gautam, A.D. Schwab, A. Dhinojwala, D. Zhang, S.M. Dougal, M.S. Yeganeh, "Molecular Structure of Polystyrene at Air/Polymer and Solid/Polymer Interfaces," Phys. Rev. Lett. 85, 3854-3857 (2000).