Abstract

1. Introduction

Plasmonics in the mid-infrared (IR) range has gained increasing attention [1,2], because of potential applications to surface-enhanced spectroscopy [3,4], chemical/bio sensing [5], thermal radiation control [6], optoelectronic circuit [7,8], nonlinear light-matter interactions [9], etc. Surface plasmons (SPs), including surface plasmon polaritons (SPPs) and localized surface plasmons (LSPs), can be excited on noble metals at mid-IR wavelengths as well as at visible wavelengths. The behaviors of metal SPs, however, vary according to operating wavelengths.

At visible wavelengths, SPPs at metal/air interfaces are closely bound to the material surface, exhibiting wavelength shortening and large Ohmic loss. At mid-IR wavelengths, on the other hand, the SPs are weakly bound to the material surface, exhibiting subtle wavelength shortening and small Ohmic loss. Therefore, materials with plasma frequencies at mid-IR wavelengths (e.g., graphene and highly-doped semiconductors [2]) are suited for applications that require subwavelength confinement in the mid-IR, but noble metals are advantageous in applications where any of small loss, long propagation length, and large electric-field enhancement in the mid-IR [2,10].

Propagation length of SPPs is an important physical quantity that characterizes plasmonic materials. First, it sets the upper limit of device size when applied to practical devices like sensors and optoelectronic circuits. Second, it is a direct measure of the Ohmic loss which underlies the degree of electric-field enhancement obtainable upon SP excitation. Here we note that the electric-field enhancement plays a key role in most of the plasmonic applications. In general, damping of SPs is composed of radiative damping and irradiative damping [11]. Radiative damping occurs by coupling with free-propagating light, and its rate strongly depends on size and shape of each metal structure. Irradiative damping, on the other hand, originates from scattering of free electrons by electrons, phonons, defects, impurities, surfaces, boundaries, etc., and is inherent to each material and its morphology. Therefore, the SPP propagation length not only provides the measures of performances in applications, but also helps us understand the physics behind the Ohmic loss.

Among noble metals, gold is an excellent plasmonic material, because of its high metallic conductivity and superior chemical stability [12]. Although there have been a report on the propagation length of mid-IR SPPs at copper/air interface [13], a report on the propagation length of visible SPPs at gold/air interface [14], and studies on IR dielectric function of gold in relation to morphology [15,16], there has been no report, to the best of our knowledge, on the propagation length of mid-IR SPPs at gold/air interface.

In this paper, we report experimental studies on propagation length of SPPs at gold/air interfaces at a mid-IR wavelength of 10.6 m. We showed that the SPPs propagates for a distance about 10 mm, in agreement with the value predicted from the dielectric constant of polycrystalline gold. In addition, we correlated the SPP propagation length with surface morphology, where surface morphology of polycrystalline gold was modified by thermal annealing and characterized by atomic force microscopy (AFM). Then, the SPP propagation length was demonstrated to increase with increased grain size and suppressed surface roughness, both of which were induced by simple thermal annealing treatment.

4. Results

Figure 4 shows AFM topography images of the waveguide surface for the sample (a), (b), and (c). The granular pattern typical for polycrystalline gold is clearly observed for the as-grown sample (Fig.4(a)). The grain size seems to increase upon annealing (see Figs. 4 (b,c)), although the grain boundaries became unclear. In any case, we estimated average grain size and average aspect ratio by using the watershed algorithm. By assuming that each grain has spherical shape, grain diameter is estimated to be 70nm, 190nm, and 180nm, for the sample (a), (b), and (c), respectively (how much is the error bar?). Aspect ratio of the grain is estimated to be 1.60.8, 2.42.5, and 2.01.8 for the sample (a), (b), and (c), respectively. By calculating root mean squares of deviations in height data, surface roughness is estimated to be 5.7 nm, 2.8 nm, and 2.2 nm (2.1 nm?) for the sample (a), (b), and (c), respectively, In this way, the thermal annealing at 600oC or above was found to increase the grain size and reduces the surface roughness.

The SPP-light coupling efficiency of the coupler grating is estimated to be 0.18 in our experiments. Although optimum incident angle for the maximum coupling efficiency shifted by about 0.5o upon annealing, the change in the achievable maximum coupling efficiency was not observed. The AFM measurements confirmed that the coupler gratings have ideal rectangular profiles before and after the annealing treatments.

5. Discussions

In the following, we discuss the physics behind the observed result that the SPP propagation length increased by thermal annealing. In general, the loss mechanism of SPs is categorized into radiative damping and irradiative damping [Link and El-Sayed 2000], but the latter is dominant in the case of SPPs at planer metal/air interfaces. The irradiative damping or the Ohmic loss originates from elastic/inelastic scattering of free electrons by electrons, phonons, defects, impurities, etc, and is reflected into the dielectric constant of metal material. It has been suggested that the smaller grain size of polycrystalline gold reduces the mean free path of free electrons, and therefore increases the imaginary part of the dielectric constant or Ohmic loss [Kuttge 2008, Olmon 2012, Trollmann and Pucci 2014]. Radiative damping of SPPs may originates from scattering of SPPs at surface roughness, grain boundaries, etc. It has been suggested that inhomogeneous spatial distribution of free electrons at grain boundaries can scatter SPPs [Kuttge 2008].

In our experiments, the increase SPP propagation length was correlated with the increased grain size and the suppressed surface roughness upon the first thermal annealing. Here we can naturally conclude that the thermal annealing increased the grain size, which reduced both of the Ohmic loss and the SPP scattering at grain boundaries. Suppressed surface roughness may also contribute to increase the propagation length to some extent, but we are not able to distinguish contribution from each origin. It would be possible to attribute the increase SPP propagation length quantitatively to each origin by simultaneous measurements of dielectric constants.

Upon the second thermal annealing at 700 oC, the SPP propagation length increased, although the average grain size did not increase. Here the increase in the SPP propagation length may be attributed to the reduced aspect ratio of the crystal grains. As the aspect ratio decreases with its average grain diameter unchanged, the grain boundary density would get smaller. It follows that the mean free path of free electrons decreases. In any case, the elongation of the propagation length by the annealing was demonstrated, which is relevant to the material morphology.

Thermal annealing is a convenient method for controlling material morphology of gold [], especially increasing grain size of polycrystalline. It has, however, minor side effect that pinholes may be generated on metal surface. In fact, pinholes with diameters of <1 m appeared with a number density of 0.16 m-2 after the first annealing process, and with a number density of 0.44 m-2 after the second annealing process. Such pinholes are much smaller than the SPP wavelength but may scatter SPPs and reduce the SPP propagation length. Although we are not able to evaluate quantitatively the SPP propagation loss due to scattering at pinholes, it would be safely concluded that the increase of the propagation length due to the morphology change was more than the decrease of the propagation length due to the pinholes.

6. Conclusions

We experimentally measured the propagation length of SPPs along gold/air interface at mid-IR range, for the first time, to the best of our knowledge. We experimentally showed that SPPs at gold/air interface propagate as long as >10mm at a wavelength of 10.6 m. The measured propagation length is in good agreement with the value predicted from the dielectric constant of polycrystalline gold. We also demonstrated that the SPP propagation length increases with the morphology change (increased monocrystalline grain size and suppressed surface roughness) induced by thermal annealing process.

Quantitative evaluation of the SPP propagation length, demonstrated in this paper, is important in designing plasmonic devices and beneficial for deeper understandings of mid-IR plasmonics.

1. R. Stanley, Nature Photon. 6, 409 (2012).

2. S. Law, V. Podolskiy, and P. Wasserman, Nanophotonics 2, 103 (2012).

3. F. Neubrech, A. Pucci, T. Walter, C. S. Karim, A. Garcia-Etxarri, and J. Aizpurua, “Resonant plasmonic and vibrational coupling in a tailored nanoantenna for infrared detection,” Phys. Rev. Lett. 101, 157403 (2008).

4. C. V. Hoang, M. Oyama, O. Saito, M. Aono, and T. Nagao, “Monitoring the presence of ionic mercury in environmental water by plasmon-enhanced infrared spectroscopy,” Sci. Rep., 3, 1175 (2013).

5. J. W. Cleary, R. E. Peale, D. Shelton, G. Boreman, and W. R. Buchwald, “Silicides for infrared surface plasmon resonance biosensors,” Proc. Mater. Res. Soc. 1133, 1133-AA10-03 (2008).

6. F. Kusunoki, J. Takahara, and I. Kobayashi, “Qualitative change of resonant peaks in thermal emission from periodic array of microcavities,” Electron. Lett. 39, 23 (2003).

7. T. W. Ebbesen, C. Genet, S. I. Bozhevolnyi, “Surface-plasmon circuitry,” Phys. Today, 61, 44, (2008).

8. R. Soref, R. E. Peale, and W. R. Buchwald, “Longwave plasmonics on doped silicon and solicides,” Opt. Exp. 16, 6507-6514 (2008).

9. F. Kusa, K. E. Echternkamp, G. Herink, C. Ropers, and S. Ashihara, “Optical field emission from

resonant gold nanorods driven by femtosecond mid-infrared pulses,” AIP Advances, 5, 077138 (2015).

10. F. Kusa and S. Ashihara, J. Appl. Phys. 116, 153103 (2014).

11. S. Link and M. A. El-Sayed, Int. Rev. Phys. Chem. 19, 409 (2000).

12. A. V. Zayats, Nature 495, S7 (2013).

13. H. Shiba, M. Haraguchi, M. Fukui, “Propagation length of surface plasmon polaritons propagating along air-metal interface,” J. Phys. Soc. Jap. 63, 1400 (1994).

14. M. Kuttge, E. J. R. Vesseur, J. Verhoeven, H. J. Lezec, H. A. Atwater, and A. Polman, “Loss mechanisms of surface plasmon polaritons on gold probed by cathodoluminescence imaging spectroscopy,” Applied Physics Letters, 93(11), 2008.

15. J. Trollmann and A. Pucci, “Infrared dielectric function of gold films in relation to their morphology,” J. Phys. Chem. C 118, 15011 (2014).

16. H. U. Yang, J. D'Archangel, M. L. Sundheimer, E. Tucker, G. D. Boreman, and M. B. Raschke, “Optical dielectric function of silver,” Phys. Rev. B 91, 235137 (2015).