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Ion beam surface nanostructuring of noble metal films with localized surface plasmon excitation

Xuan Meng [a,b], Tamaki Shibayama [a,*], Ruixuan Yu [a], Junya Ishioka [a], Seiichi Watanabe [a]

[a] Center for Advanced Research of Energy and Materials, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
[b] School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China

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ABSTRACT

Noble metal nanoparticles strongly adhered to dielectric matrices have been extensively studied because of their potential applications in plasmonic devices based on tunable localized surface plasmon (LSP) excitation. Compared with conventional synthesis methods, the noble metal nanoparticles formed by ion-beam irradiation draw significant interest in recent years because a single layer dispersion of nanoparticles strongly bonded on the dielectric substrate can be obtained. In this paper, important phenomena related to ion-beam surface nanostructuring including ion-induced reshaping of metal nanoparticles, ion-induced core-satellite structure formation, and ion-induced burrowing of these nanoparticles are discussed, with their individual effects on LSP excitation. Consequently, ion-induced surface nanostructuring of Ag-Au bimetallic films on amorphous silica glass and sapphire with tunable LSP excitation are presented. In addition, theoretical studies of far-field and near-field optical properties of these nanoparticles under ion irradiation are introduced, and the enhanced localized electric field (hot spot) is interpreted. Finally, the futures and challenges of the emerging plasmonic applications based on tunable LSP excitations in bio-sensing and surface enhanced Raman spectroscopy (SERS) are presented.

1. Introduction

Physical and chemical properties of low-dimensional solid-state systems have attracted considerable attention because of their technological significance [1–4]. A striking feature of modern technology is the important role of the surface and near-surface regions of materials. Specifically, metal nanostructures with sub-micrometer dimensions exhibit very different optical responses with respect to their bulk counterparts [2–7]. In the past decade, metallic nanoparticles either sustained on the surfaces or dispersed in dielectric matrices have been extensively studied experimentally as well as theoretically because of their pronounced optical and electrical properties [1–7]. An external electromagnetic (EM) field can penetrate inside the volume of the particles, shifting the free electrons gas with respect to the ion lattice; consequently, polarizing the metal and establishing restoring local fields. Under resonance conditions, the free electrons gas is coherently dragged by the external excitation, so the electric dipoles induced inside each particle become extremely large. Correspondingly, the local fields in proximity of the particles are orders of magnitude enhanced with respect to the incident fields, and very strong absorption peaks in photoabsorption spectra are observed. Such collective excitations are commonly known as localized surface plasmon resonance (LSPR) [2–5]. For noble metal nanostructures, the localized surface plasmon (LSP) excitations are usually observed in the visible range (Cu, Ag and Au). Nowadays, there are many interests in synthesizing silica glass based metal-silica nanocomposites for their appreciable applications in plasmonics such as surface enhanced Raman spectroscopy (SERS) and recent development in tip-enhanced Raman spectroscopy (TERS) [8–10], and LSPR-based biosensor [11–13].

Nowadays, colloidal chemistry can produce a myriad of metal nanoparticles (NPs) in solutions with a variety of morphologies from spherical to complex core-shell, with very good control of the size distribution [8,10,14,15]. This control over the size, composition, and morphology of the NPs in a system can produce dramatically different absorption features in the visible or near-infrared spectrum. Examples of Au nanocrystals fabricated using colloidal chemistry techniques are presented in Fig. 1. They illustrate how particle shape influences the photo extinction spectra [15]. In addition, by changing the nanosphere diameter and the deposited metal thickness, nanoparticles with different in-plane width, out-of-plane height and interparticle spacing can be produced by the nanosphere lithography technique [11,12,16]. However, the nanostructures fabricated by this technique have weak

* Corresponding author.
E-mail address: shiba@qe.eng.hokudai.ac.jp (T. Shibayama).

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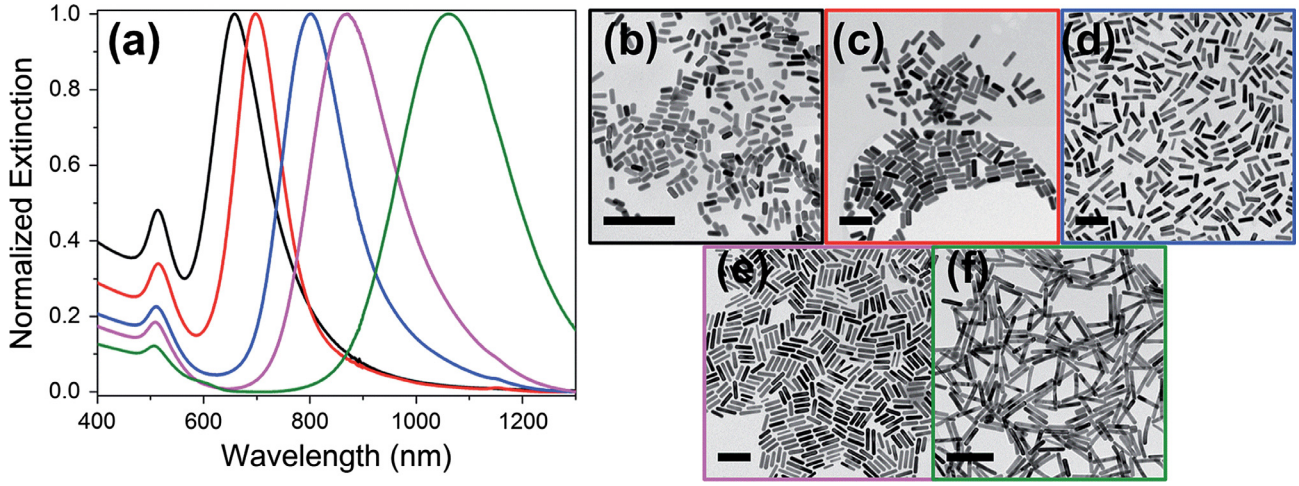

Fig. 1. (a) Normalized extinction spectra for gold nanorods with different aspect ratios. The black, red, blue, magenta, and green spectra were taken for gold nanorods with aspect ratios 2.4, 2.7, 3.6, 4.4, and 6.1, respectively, with corresponding TEM images in (b)–(f). Scale bars are 150 nm [15]. Adapted from J. G. Hinman, A. J. Stork, J. A. Varnell, A. A. Gewirth and C. J. Murphy, Seed mediated growth of gold nanorods: towards nanorod matryoshkas, Faraday Discuss., 191 (2016) Pages 9–33, with permission of The Royal Society of Chemistry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

adhesion with the substrate. The inherent limitations render the applications in solid-state devices difficult to attain for the standard nanostructuring techniques, like colloidal chemistry (CS) and nanosphere lithography (NL) [6,7]. To overcome these limitations, several alternative strategies have been developed including laser lithography [17,18], electron beam lithography [19,20], and focused ion beam (FIB) milling [21,22]. Among them, ion-beam irradiation represents an innovative approach to tune the morphology of nanostructured materials.

Ion-beam technology provides a unique and exciting way to modify the near-surface region of a solid, and provides a level of control and specificity that exceeds almost all the other methods in surface modification [21–26]. The most obvious phenomena are the ion-induced local melting [27–29], sputtering [30–34], dewetting of thin films [35–39], ion-induced reshaping of nanostructures [40–44], and ion-enhanced burrowing of nanostructures into the viscous substrate [44–48]. The importance of this subject matter does not uniquely reside in its fundamental interest but also in the possibility to engineer systems containing nanostructures in configurations that are nearly impossible to obtain by other techniques, in which morphologies of the metallic nanostructures can be tuned by varying the irradiation conditions (ion type, energy and fluence) [21–28,30–39,47,48]. Up to now, many works on ion-beam surface nanostructuring represents a step forward in the development of an alternative route, with respect to standard colloidal chemistry and nanolithography techniques, to the controllable fabrication of a whole family of nanostructures with tunable optical and electronic properties [21,23–26,40,44,47,48]. In this review, the phenomena related ion-beam surface nanostructuring are described first, including ion-induced dewetting of thin films (Section 2.1), ion-induced reshaping of nanostructures (Section 2.2), and ion-enhanced burrowing of nanostructures into the viscous substrate (Section 2.3). The optical responses of Ag-Au bimetallic nanostructures under ion irradiation are described in Section 3. Following this, future opportunities and emerging device applications of plasmonic nanostructrues are presented (Section 4). Finally, future directions and outlook are proposed in Section 5.

2. Metal nanostructure synthesis by ion irradiation

Ion irradiation of thin solid films can induce surface morphologies that differ substantially from the outcome observed in the case of bulk samples. The interaction of energetic ions with solid surfaces has been studied for more than 60 years and for many combinations of ion and solid the energy deposition process is reasonably well known and understood [27–36]. One of the most striking examples of changes in the surface topology during ion bombardment is the production of holes and craters, which has been observed *in situ* with 200 keV Xe and Kr ion impactions on very thin Au films at room temperature [27,28]. Theoretically, molecular dynamics (MD) modeling of the impact of a 20 keV Au ion on an Au surface indicates a large amount of plastic deformation on the Au surface, and the calculated topography resulting from the deformation and outflow may give rise to a permanent crater [29]. It is therefore concluded that changes in morphology during irradiation is attributed to a localized, thermal-spike induced melting, coupled with plastic flow under the influence of surface forces. In addition, during the quenching phase of the molten zone, surface tensions will act on any free surfaces involved within the melt zone. This gives rise to the overall tendency for holes to enlarge [30–34]. The maximum radius (r_m^0) of the induced molten zone leading to crater formation was roughly estimated using the following relation [30,31]: $r_m^0 = (E_D^0/\pi n_0 \varepsilon_m)^{1/2}$, where, E_D^0 is the deposited energy per unit length along the ion path, n_0 is the atomic density of the metal and $\varepsilon_m (\approx 3\,kT_m)$ is the average energy of the atom at the melting temperature T_m. For example, the molten zone induced by 800 keV Kr ion irradiation of thin Pt films was estimated to be 5 nm [30], and the molten zone induced by 150 keV Ar ion on thin Au films was estimated to be 3 nm [31].

On the other hand, in the process of ion irradiation, the incident ions penetrate into the target and transfer their kinetic energy to the target atoms by creating a cascade of collisions among the substrate atoms or through other processes such as electronic excitations [32,34–36]. Most of these atoms will come back to their original lattice sites but some of them, especially those atoms located in the first layer or two of the surface that receive recoil energies greater than the sublimation energy (~5 eV) with momentum directed away from the surface can be sputtered into the vacuum [37–39]. As a consequence, the surface continually erodes during irradiation. The amount of erosion is measured by the sputtering yield, which is defined as the mean number of atoms removed from the surface of a solid per incident particle [35,36]. For amorphous and polycrystalline targets, Sigmund revealed that the sputtering yield is proportional to the energy accumulated in the near surface [35]. More importantly, Sigmund

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