SERS substrates by vacuum-free dealloying of Au-based metallic glass ribbons

Plasmonics has become an important photonic device due to the advancement of fabrication technologies in recent decades. It has many applications including solar cells, nonlinear optics, metamaterials, photocatalysts, and surface-enhanced Raman spectroscopy (SERS), etc. Among those, SERS is a promising technique for molecular detections because the molecular structures can be precisely identified via the considerable amplification of Raman intensity by localized surface plasmon resonance (LSPR), and it has been used in many applications, such as biosensing, chemical imaging, and single molecule detection.

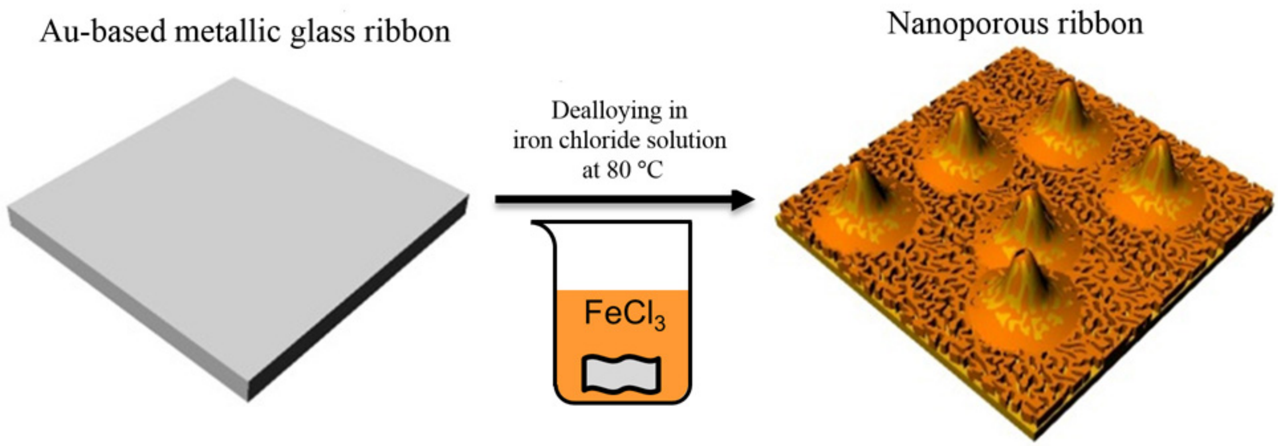

Fig. 1. Schematic drawing of dealloying of Au-based metallic glass ribbon. Au55Cu25Si20 metallic glass ribbons were used to fabricate Au-rich SERS substrates by chemical dealloying in the iron chloride solution at 80 ºC for 30 min.

For SERS, the resonance wavelength strongly depends on the surrounding medium and the size and shape of metallic nanostructures of SERS substrates. By using ion lithography or e-beam lithography, precise nanostructures can be fabricated. However, both lithographies are high-cost and low fabrication efficiency, which become the main limitations of mass production. Therefore, some random nanostructures have been used for SERS substrates, such as nanopillar and nanoporous substrates. Nevertheless, most of the fabrication processes for nanopillar and nanoporous substrates need to use the high-cost vacuum system and are ineffective for mass production. To avoid using the vacuum system, dealloying homogeneous alloy sheet is a low-cost means to fabricate nanoporous substrates. Through removing selected metals from the alloy, the remaining metallic nanoporous structure can be obtained. For SERS applications, by selectively leaching out Ag in the Ag-Au single phase alloy sheet, nanoporous Au sheet could be prepared. These fine interstices in the nanoporous structure can serve as hot spots due to near-field coupling of LSPR, and it has demonstrated large SERS enhancements.

Metallic glass is one of the homogeneous metal materials with an amorphous structure. By rapidly quenching the melt to below its glass transition temperature, the frozen atoms promptly solidifies before crystallization. Thus, the amorphous structure can be achieved without crystalline defects and it results in high strength and large elastic strain limit. In addition to the excellent mechanical properties, this amorphous alloy also has the potential for dealloying. Compared with dealloying of crystalline alloys, dealloying of metallic glasses would yield a more uniform nanoporous structure because metallic glasses are free from grain boundaries and other crystalline defects. Au-based metallic glass was the first reported amorphous alloy which could be a good raw material to fabricate Au nanoporous substrate by removing other elements.

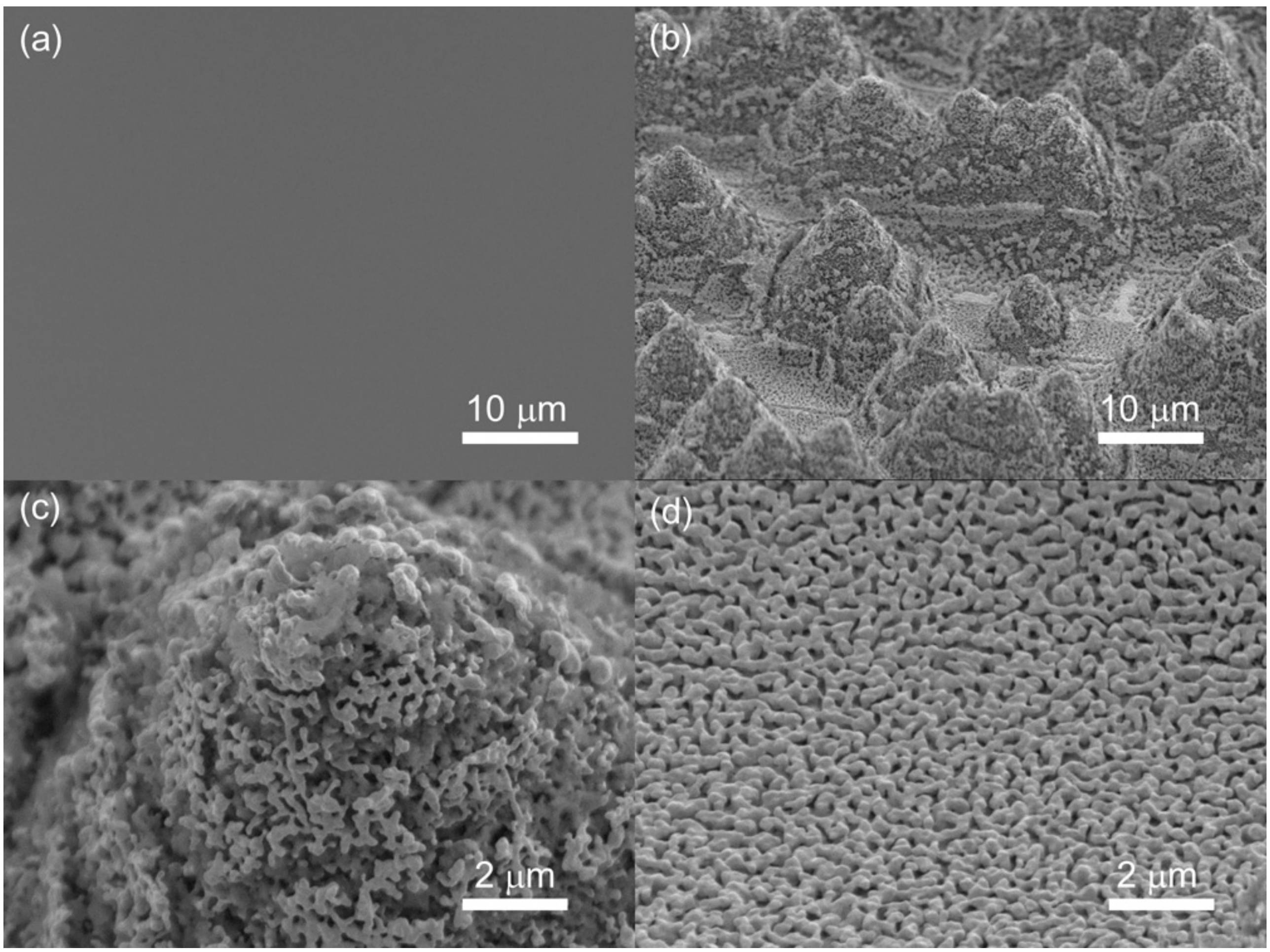

Fig. 2. Surface morphologies of Au-based materials. (a) Untreated Au-based metallic glass ribbon, (b) dealloyed Au-based metallic glass ribbon, and the enlarged (c) micro-island region and (d) valley region of the dealloyed ligament structure.

In this work, we developed a new method to fabricate a vacuum-free, high surface area, Au-rich interconnected ligament substrate by dealloying the Au-based metallic glass ribbon (Au-Cu-Si system) for SERS applications. This was the collaborative work between National Taiwan University team led by Prof. Hsueh and City University of Hong Kong team led by Prof. Shek. The schematic drawing of dealloying of Au-based metallic glass ribbon is shown Figgure 1. The plane-view of untreated Au-based metallic glass ribbon shown in Figure 2(a) revealed a flat surface. After dealloying, the Au-based material showed ligament nanostructure with protruding micro-islands in Figure 2(b). The enlarged micro-island and flat valley region are shown, respectively, in Figure 2(c) and (d). The micro-island with a larger surface area could adsorb more analyte molecules for SERS enhancements. Based on the field emission scanning electron microscopy, reflection and scattering measurements, the dealloyed Au-based metallic glass provided a large surface area, multiple reflections, and numerous fine interstices to produce hot spots for SERS enhancements. Specifically, the SERS signal of analyte, *p*-aminothiophenol, in the micro-island region of dealloyed Au-based metallic glass was about 2 orders of magnitude larger than the flat Au film. Our work provides a new method to fabricate the inexpensive, vacuum-free, and high SERS enhancements substrates.

Chun-Hway Hsueh
Department of Materials Science and Engineering
National Taiwan University, Taiwan

Publication

[Gold-rich ligament nanostructure by dealloying Au-based metallic glass ribbon for surface-enhanced Raman scattering.]
Chao BK, Xu Y, Ho HC, Yiu P, Lai YC, Shek CH, Hsueh CH
Sci Rep. 2017 Aug 8