

In-situ Observation of Alloy Phase Formation in Isolated Nanometer-sized Particles

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Understanding the structure (or phase) stability of nm-sized condensed matter is one of the key issues in advancing materials reliability in a broad spectrum of nanotechnologies including microelectronics technologies. To the authors' knowledge, however, studies on the phase stability in nm-sized particles, particularly in alloy particles, are limited. Based upon this premise, in the present work, alloy phase formation in nm-sized particles has been studied by in-situ transmission electron microscopy, using particles in the Au-Sn and Sn-In systems [1-3].

Preparation of gold particles and subsequent vapor-deposition of tin onto gold particles was carried out using a miniature double-source evaporator that was set at the tip of a side-entry specimen holder. The evaporator essentially consisted of two spiral-shaped tungsten filaments. An amorphous carbon film was used as a supporting film and was mounted on a copper grid. Using this evaporator, gold was first evaporated onto an amorphous carbon film, and nm-sized gold particles were produced. Tin was then evaporated from the second source onto gold particles on the film kept at ambient temperature. Changes in the structure and chemical composition of particles associated with the tin deposition were studied. The chemical composition of individual particles on the film was analyzed by energy dispersive X-ray spectroscopy (EDS). The microscope used was a Hitachi HF-2000 TEM equipped with a field emission gun, operating at an accelerating voltage of 200 kV. The base pressure in the specimen chamber was below 5×10^{-7} Pa. Alloy formation in the Sn-In system was examined in a similar way.

When tin atoms were vapor-deposited onto nm-sized gold particles, rapid dissolution of tin atoms into gold particles took place and as a result of this, particles of an Au-rich fcc solid solution alloy, of a topologically-disordered amorphous alloy, and of the AuSn compound were formed with increasing concentration of tin. Figure 1 shows examples of high-resolution images (HRIs) taken from these alloy particles, with the corresponding EDS spectra. Each EDS spectrum was obtained from the region encircled in each figure.

Figure 1(a) shows an HRI of an Au-18at%Sn alloy particle and the corresponding EDS spectrum. The diameter of the particle is approximately 5 nm. In Fig. 1(a), there appear lattice fringes with a spacing of 0.24 nm. The spacing is very close to the (111) lattice spacing (i.e. 0.239 nm) of fcc Au-18at%Sn solid solution. This fact suggests that the particle is an Au-Sn solid solution and that the solid solubility of tin in nm-sized gold particles amounts to at least 18 at%Sn, which is much higher than that in bulk gold (i.e. ca. 3 at%Sn at room temperature). HRIs taken from Au-32at%Sn and Au-40at%Sn alloy particles are shown in Fig. 1(b) and 1(c), respectively. The diameter of these particles is approximately 6 nm. Both particles exhibit a contrast similar to the salt and pepper contrast characteristic of topologically-disordered materials. This observation indicates that a topologically-disordered, amorphous phase is produced in 6 nm-sized alloy particles in the composition range from 32 to 40 at%Sn. Figures 1(d) and 1(e) show HRIs of approximately 8 nm-sized AuSn compound particles with different chemical compositions. Both compound particles are single crystalline. The 0.31 nm- and 0.37 nm-spaced fringes in the images are the (011) and (100) lattice fringes of AuSn, respectively. EDS spectra in Figs. 1(d) and 1(e) indicate that the tin concentrations of particles are 46 at%Sn (which is by ca. 4 at% lower than the stoichiometric composition of AuSn) and 59 at%Sn (which is by ca. 9 at% higher than the stoichiometric composition of AuSn), respectively. From this result, it is evident that remarkable enhancement of

solubility has been induced in AuSn compound particles, as compared with that in the corresponding bulk AuSn which is a line compound.

As mentioned above, in the Au-Sn system, a topologically-disordered, amorphous phase is produced in particles in the composition range from 32 to 40 at%Sn, when the size of particles is smaller than about 6 nm. A separate annealing experiment has revealed that the topologically-disordered, amorphous phase goes to melt with no preceding crystallization upon heating and the melt solidifies into the topologically-disordered, amorphous phase without any traces of crystallization upon cooling. This fact indicates that the phase is not a non-equilibrium phase. In this context, the phase is different from such non-equilibrium amorphous phases as those produced in bulk materials. It is interesting to note here that the composition range is very close to the bottom of the deep valley of the liquidus in the middle of the Au_5Sn -AuSn two-phase region in the phase diagram for the bulk material. On the other hand, in the Sn-In system, liquid alloy particles were formed over a composition range near the eutectic composition, when the size of particles is smaller than about 10nm in diameter. When the size of particles is larger than these critical values, an essentially similar phase equilibrium was observed in nm-sized particles and bulk materials in the both systems. The formation of the amorphous and liquid phase in nm-sized alloy particles can be explained in terms of the large suppression of the eutectic temperature associated with the size reduction.

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References

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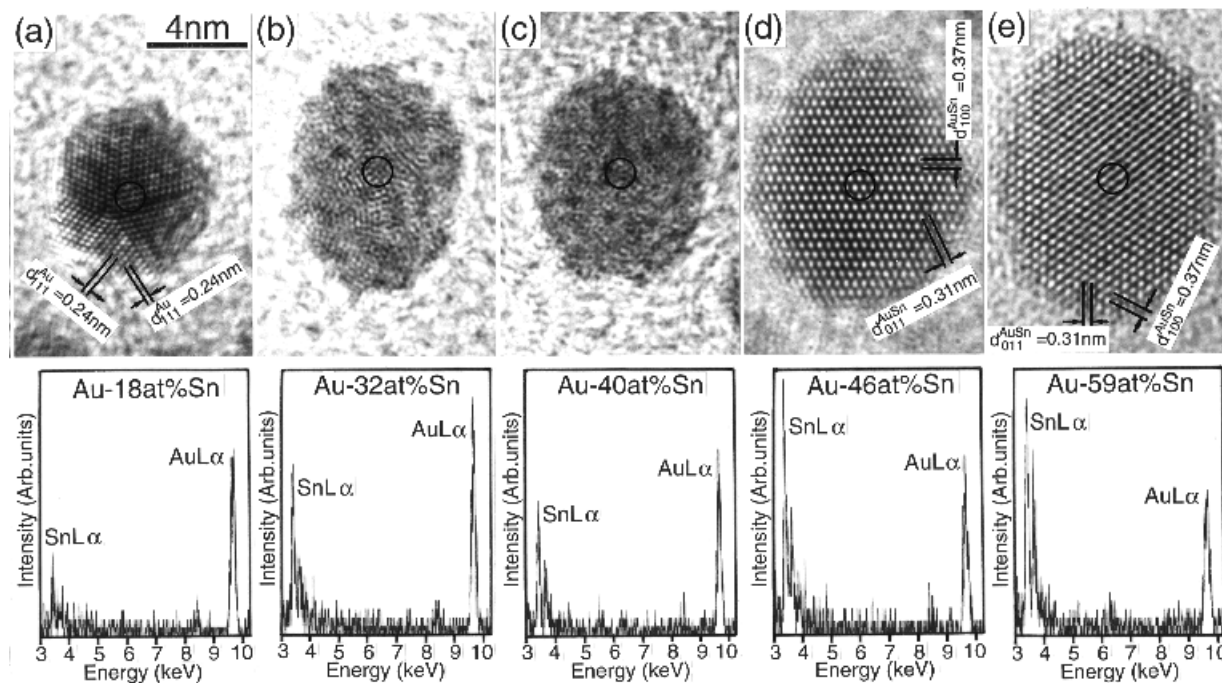


FIG.1. High resolution images of Au-Sn alloy particles and the corresponding EDS spectra taken from the region encircled. (a) Au -18at%Sn alloy particle, (b) Au-32at%Sn alloy particle, (c) Au-40at%Sn alloy particle, (d) Au-46at%Sn alloy particle, (e) Au-59at%Sn alloy particle.