

# Characterization of the microstructure and phase formation in the Au–In system using transmission electron microscopy

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## Abstract

The Au–In system is of both fundamental and technical importance for engineering applications such as microelectronic packaging. The growth mechanism and crystal orientation of the Au and In thin films produced by thermal evaporation on NaCl substrates are studied by transmission electron microscopy (TEM). Like most metals, the growth of both Au and In thin films on single crystals of NaCl follows the Volmer–Weber mode, i.e. formation of metal nuclei first, and then grain growth and coalescence of the particles to form a continuous thin film. In contrast, the growth of In on the Au-coated NaCl substrates follows the Frank–van der Merwe mode, i.e. layer by layer, as a result of strong interactions between Au and In. The formation of AuIn<sub>2</sub> phase occurs instantly upon In deposition, and the intermetallic exhibits an epitaxial orientation to the underlayer Au single crystals. In addition, cross-section TEM observation of the Au/In/Au thin sections by ultramicrotomy shows that the AuIn<sub>2</sub> intermetallic is brittle. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Growth mechanism; Intermetallic; Microstructure; Transmission electron microscopy

## 1. Introduction

The study of metallic thin films is of both technological importance and fundamental interest. On one hand, thin films are the key technology in many sectors of hi-tech industry, e.g. in the manufacturing of microelectronics components and solid state devices [1,2], on the other hand, they often show properties that differ from the bulk [3,4], e.g. the solubility of an impurity in a thin film is usually much higher than that in the bulk. In many applications, different types of metallic thin films need to be prepared for specific purposes. As a result, an understanding of the interactions among metals and the formation of intermetallics and their properties are crucial for the design and fabrication of solid-state devices involving thin film technology.

In a recent research conducted by Shimizu et al. [5], it is demonstrated that indium (In)-containing alloy solders have longer fatigue life, better mechanical properties and reliability than conventional tin (Sn)-containing alloys as solder interconnections for electronic packaging. Other desired properties such as thermal stability and corrosion resistance of the In-containing alloys are also reported [6–8]. It is, therefore, expected that In-containing alloys may be used in the surface mount technology for microelectronics devices

in the near future. Unlike indium, gold (Au) is being widely used in the electronic industry as contact and conductor material. Reactions and characteristics of a metal–In micro-joint such as Au–In need to be investigated in great detail before the engineering practice of the In-containing solders can become useful. One particular technology, so-called solid–liquid interdiffusion bonding (SLID) [9] that is drawing great attention currently for joining the die and substrate in microelectronics packaging, involves the preparation of two or more metallic thin films. One key parameter for the success of the SLID technology is control of the thickness of the metallic thin films properly.

In this study, the growth modes of Au and In thin films prepared by thermal evaporation using electrical resistance heating are investigated. Formation and mechanical properties of the AuIn<sub>2</sub> intermetallic from the Au–In bilayer are characterized by transmission electron microscopy (TEM). In addition, the effect of the Au interlayer on the orientation relationships of the In thin films deposited on the NaCl substrate, and the formation of texture in the In of the Au–In microjoints upon shear loading are discussed.

## 2. Experimental

Two types of specimens with different geometry were prepared to study the reactions between Au and In. In one type, single crystals of NaCl cleaved along (001) plane were

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used as the substrate, in which Au thin films of thickness about 50 nm were first deposited on the substrate by thermal evaporation using a resistance-heated W boat. Subsequently, a thin In film of thickness about 20 nm was deposited onto the aforementioned Au-coated NaCl substrate to form an In/Au bilayer structure. The base pressure of the vacuum chamber before evaporation is  $\sim 1.1 \times 10^{-3}$  Pa, and rises up to  $\sim 2.7 \times 10^{-3}$  Pa during deposition. A quartz-type thickness monitor was used to measure the deposition rate, and the thickness of Au and In thin films.

In the second type of specimens, a thick Au layer of about 5  $\mu\text{m}$  using thermal evaporation was deposited onto a polyethylene terephthalate (PET) substrate of dimensions 5 mm  $\times$  10 mm  $\times$  0.2 mm. Specimens for tensile test were made by sandwiching an In foil of 20  $\mu\text{m}$  thick between the Au-coated PETs, and then hot-pressed in air at 250°C for 5 min. The shear strength of the Au/In/Au microjoints was evaluated by a single lap tensile test.

Microstructure of the two types of specimens was characterized by a Zeiss 902A energy filtering TEM operated at 80 kV. For the first type of specimens, thin sections were prepared by dissolving the single crystals of NaCl in distilled water and then picked up by a 300 mesh Cu grid [10]. In cases where the deposition time is short corresponding to the early stage of film growth and thus the metal film is discontinuous, a thin layer of carbon is evaporated onto the metal-coated NaCl substrates before dissolving in the water. For the sandwiched Au/In/Au specimen that has undergone tensile loading, thin sections of the failure components about 100 nm thick for cross-section TEM observation were made by a Reichert Ultracut E ultramicrotome.

### 3. Results and discussion

#### 3.1. Growth of Au and In thin films on NaCl substrates

The growth modes of metallic thin films on a substrate can, in general, be classified into three categories: the

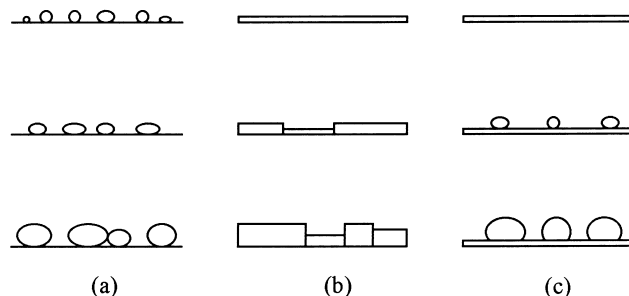


Fig. 1. A schematic of the three growth modes commonly occurring in the vapor deposition of metallic thin films: (a) Volmer–Weber mode; (b) Frank–van der Merwe mode, and (c) Stranski–Krastanov mode.

Volmer–Weber mode, the Frank–van der Merwe mode and the Stranski–Krastanov mode, as shown in Fig. 1 [11]. The first mode usually occurs when the surface energy of the film materials is large compared with that of the substrate. The second and third modes, on the other hand, take place when a film of low surface energy is deposited on a substrate of high surface energy. If the strain energy in the film is small compared with the surface energy of the film material, the film will grow by the Frank–van der Merwe mechanism; if the strain energy in the film, however, is large, the Stranski–Krastanov mode will dominate.

Fig. 2(a) and (b) show the morphology of Au particles deposited on a single crystal of NaCl substrate by thermal evaporation for 10 and 30 s, respectively. It can be seen from the micrograph of Fig. 2(a) that discrete Au nuclei with particle sizes ranging from 1 to 3 nm are formed at the early stage of deposition and then coalescence of the Au particles, shown in Fig. 2(b), gradually occurs as deposition continues. The Au particles grow both laterally and vertically, and eventually a continuous film of 50 nm is obtained as shown in Fig. 3(a). The bright disk-like areas in the image, within which extinction contours with four-fold symmetry are observed, reflect that the cleaved NaCl surface is full of

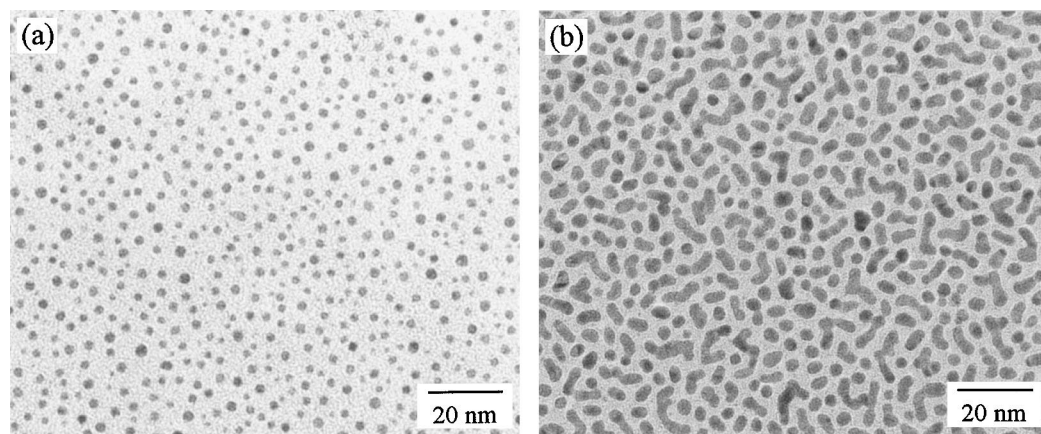


Fig. 2. Evolution of the Au thin film on single crystals of NaCl substrate during early stage of thermal evaporation: (a) formation of Au nuclei, and (b) coalescence of the Au particles upon deposition for 10 and 30 s, respectively.

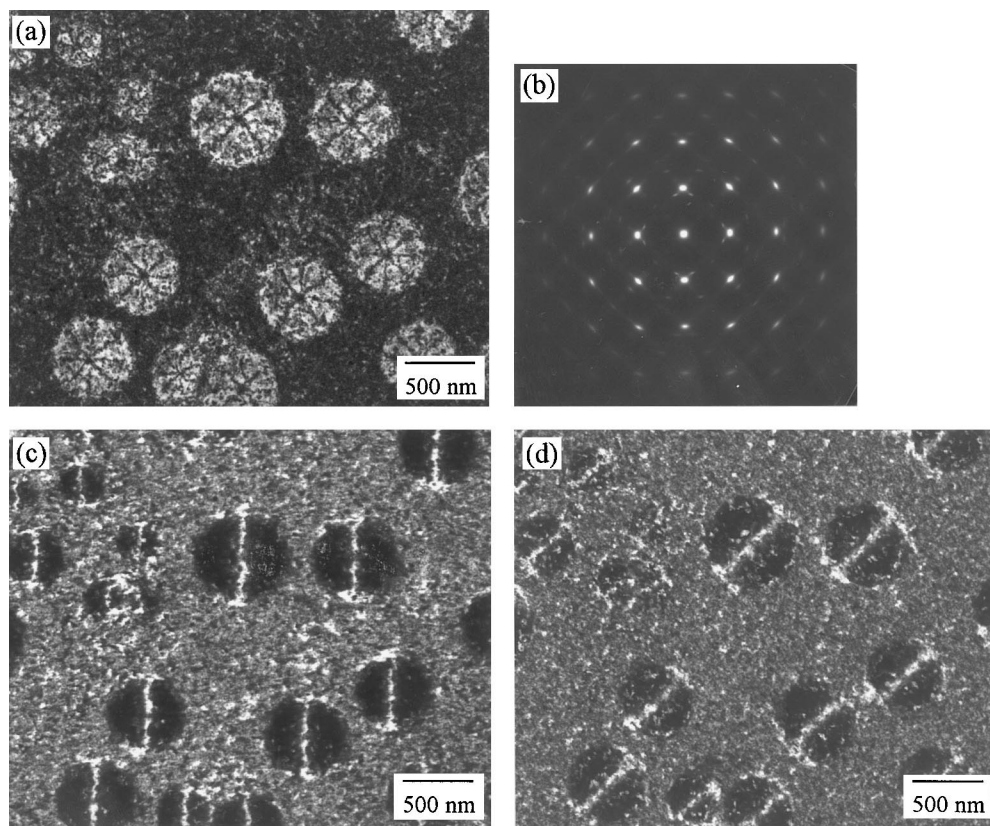


Fig. 3. TEM micrographs showing (a) the BF image, (b) the SAD pattern, (c) the (200) DF, and (d) (220) DF images, of a continuous Au film deposited on the NaCl substrate. The appearance of the bright disk-like areas in the images reflect many protrusion defects on the substrate surface.

protrusion defects [12]. A selected area diffraction (SAD) pattern of the thin film is given in Fig. 3(b), which reveals that the Au layer has an epitaxial orientation relationship with the single crystal of NaCl substrate, i.e.  $(001)_{\text{Au}} // (001)_{\text{NaCl}}$  and  $[001]_{\text{Au}} // [001]_{\text{NaCl}}$ . The dark field (DF) images using (200) and (220) reflections are shown in Fig. 3(c) and (d), respectively, where the intersection of the two extinction contours resulting in an absorption

band is easily discerned. Although the microtwins in the Au thin film are not readily defined in the bright field (BF) image of Fig. 3(a), the SAD pattern of Fig. 3(b) reveals clearly the presence of strong twin spots [12].

The BF image and SAD pattern of an In thin film of thickness of about 50 nm produced by a similar deposition condition as the Au thin film shown in Fig. 3(a) are given in Fig. 4(a) and (b). In spite of the fact that the growth mode of

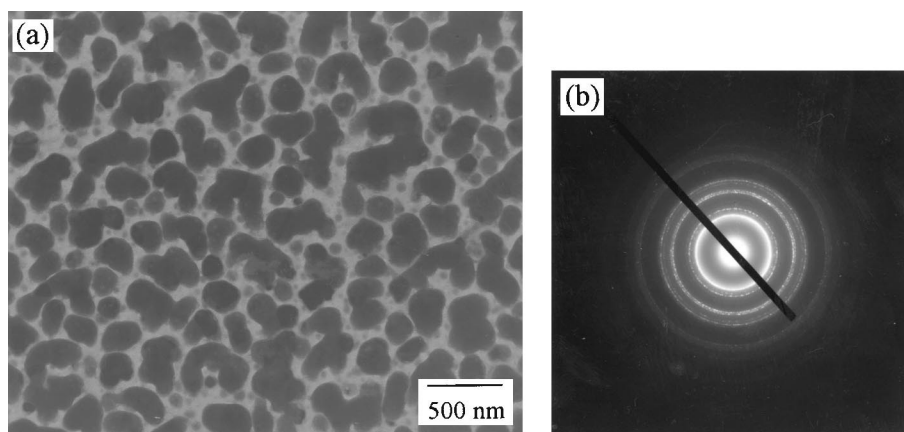


Fig. 4. TEM micrographs showing (a) the BF image, and (b) the SAD pattern of the In film having thickness similar to the Au film shown in Fig. 3, deposited on single crystals of NaCl substrate.

In on the single crystals of NaCl is similar to that of the Au on NaCl, two major differences are noted. First, within the detection limit of the thickness monitor, Au forms a continuous film but not In for the same coating thickness of 50 nm. This result is due to the surface energy of Au,  $1.185 \text{ J m}^{-2}$ , which is much higher than that of In,  $0.556 \text{ J m}^{-2}$  [13], as mentioned in the beginning of the section. As a result, the apparent growth rate of Au particles in the lateral direction is faster than that of In to reduce the total free energy of the thin film. From the cross-section viewpoint, the In particles tend to approach a sphere, whereas the Au particles favor an ellipsoid and thus form a continuous film earlier. The difference in the morphology of the metal particles is also reflected in the visibility of the microstructure of the films to the electron beam. The internal structure of the Au films can be seen in the BF image of Fig. 3(a), whereas it is almost opaque to the electron beam for the In films prepared under the same deposition condition (see Fig. 4(a)). It makes the picture even clear when the atomic scattering factor, of which the scattering power of Au is higher than that of In [12], is taken into account.

In addition, from the SAD pattern of Fig. 3(b), it is shown that the Au film is an epitaxial layer with the (001) zone axis parallel to the electron beam direction, however, the ring pattern in the selected diffraction of the In film, Fig. 4(b), indicates that it is polycrystalline. Since the lattice mismatch between In and NaCl, 42%, is much larger than that between Au and NaCl, 28%, so does the strain energy in the In thin film [11], the formation of an epitaxial relationship between In and NaCl is very likely to be obstructed.

### 3.2. Effect of the Au interlayer on the growth of In on NaCl substrates

Although the growth mode of both Au and In thin films on the single crystals of NaCl follows the Volmer–Weber mechanism, In undergoes a completely different growth mechanism on the Au-coated NaCl substrates. As mentioned in Section 3.1, the Au film of 50 nm thickness deposited on the single crystal of NaCl forms a continuous layer and exhibits an epitaxial orientation to the (001) NaCl substrate, i.e.  $(001)_{\text{Au}} // (001)_{\text{NaCl}}$  and  $[001]_{\text{Au}} // [001]_{\text{NaCl}}$ , as shown in Fig. 3. The BF image and the SAD pattern of the specimen in which In of thickness of about 15 nm was deposited on the Au-coated NaCl are given in Fig. 5(a) and (b), respectively. From the electron micrographs, it can be seen that the image contrast and features of the Au in Fig. 3(a) and the In/Au bilayer in Fig. 5(a), look very similar, except that the size of disks decreases slightly in the latter case. Since the microstructure of the two specimens remains almost unchanged before and after In was deposited onto the Au films, it strongly suggests that the In must grow on the Au surface by a mechanism of Frank–van der Merwe mode, i.e. layer by layer.

Compared with the SAD pattern of Fig. 3(b) in which Au was deposited on a single crystal of NaCl, the diffraction

pattern of Fig. 5(b) for In deposited onto the Au-coated NaCl is very complicated, and contains many extra spots. By careful analysis, it is found that the extra spots consist of reflections from the intermetallic phase  $\text{AuIn}_2$ , instead of pure In, and those due to double diffraction and microtwin, in addition to those resulting from the Au layer observed in Fig. 3(b). A close examination of the diffraction pattern in Fig. 5(b) also reveals that the (220) reflections of the  $\text{AuIn}_2$  intermetallic are nearly superimposed on the Au microtwin spots. An enlargement of the microtwin reflection showing the doublet is given in the up-right corner of Fig. 5(b). Analysis of the diffraction pattern indicates that an epitaxial relationship,  $[400]_{\text{AuIn}_2} // [220]_{\text{Au}}$  and  $[220]_{\text{AuIn}_2}$  is  $\sim 7.5$  away from  $[200]_{\text{Au}}$ , exists between  $\text{AuIn}_2$  and Au, in which  $\text{AuIn}_2$  has  $\text{CaF}_2$  type face-centered cubic structure. A schematic of the diffraction pattern illustrating the major reflections is given in Fig. 5(c).

The instant formation of  $\text{AuIn}_2$  intermetallic right after deposition of In onto Au is also observed by other investigators [14,15]. Bjontegaard et al. [14] reported that the formation and growth of  $\text{AuIn}_2$  intermetallic after evaporation is characterized by an activation energy of 0.23 eV, and that the  $\text{AuIn}_2$  phase is known to be the fastest transformation requiring the least thermal energy of any intermetallic among transition metals. In a study of In deposition on the Au (111) surface conducted by Robinson and Slavin [15] using Auger electron spectroscopy, it was found that the  $\text{AuIn}_2$  phase was formed from the onset of deposition, and the intermetallic thickened a layer at a time, i.e. following the Frank–van der Merwe mode. In addition, the growth mode of Sn deposited onto the Au surface was investigated by Zhang and Slavin [16] using Auger electron spectroscopy, low energy electron diffraction and electron energy loss spectroscopy. It was concluded that Sn initially formed an intermetallic,  $\text{AuSn}$ , which grew laterally as a double layer, followed by continued growth of the same phase one layer at a time, i.e. the Frank–van der Merwe mode [11]. From the current experimental results and those reported in the literature, it is quite clear that strong chemical reactions or alloying among overlayers favor the Frank–van der Merwe growth mode.

### 3.3. Cross-section TEM of the Au/In/Au microjoints

Since the reactions between Au and In occur even at room temperature [17], preparation of thin sections for cross-section TEM investigation by conventional ion milling method has been found to be invalid due to ion beam-induced phase transformation. To overcome this difficulty, ultramicrotomy was utilized in the current study to produce thin sections of the microjoints for TEM observation.

A cross-section TEM micrograph of the Au/In/Au microjoint after the single lap tensile test is shown in Fig. 6(a), which is composed of a region of equiaxial grains and a

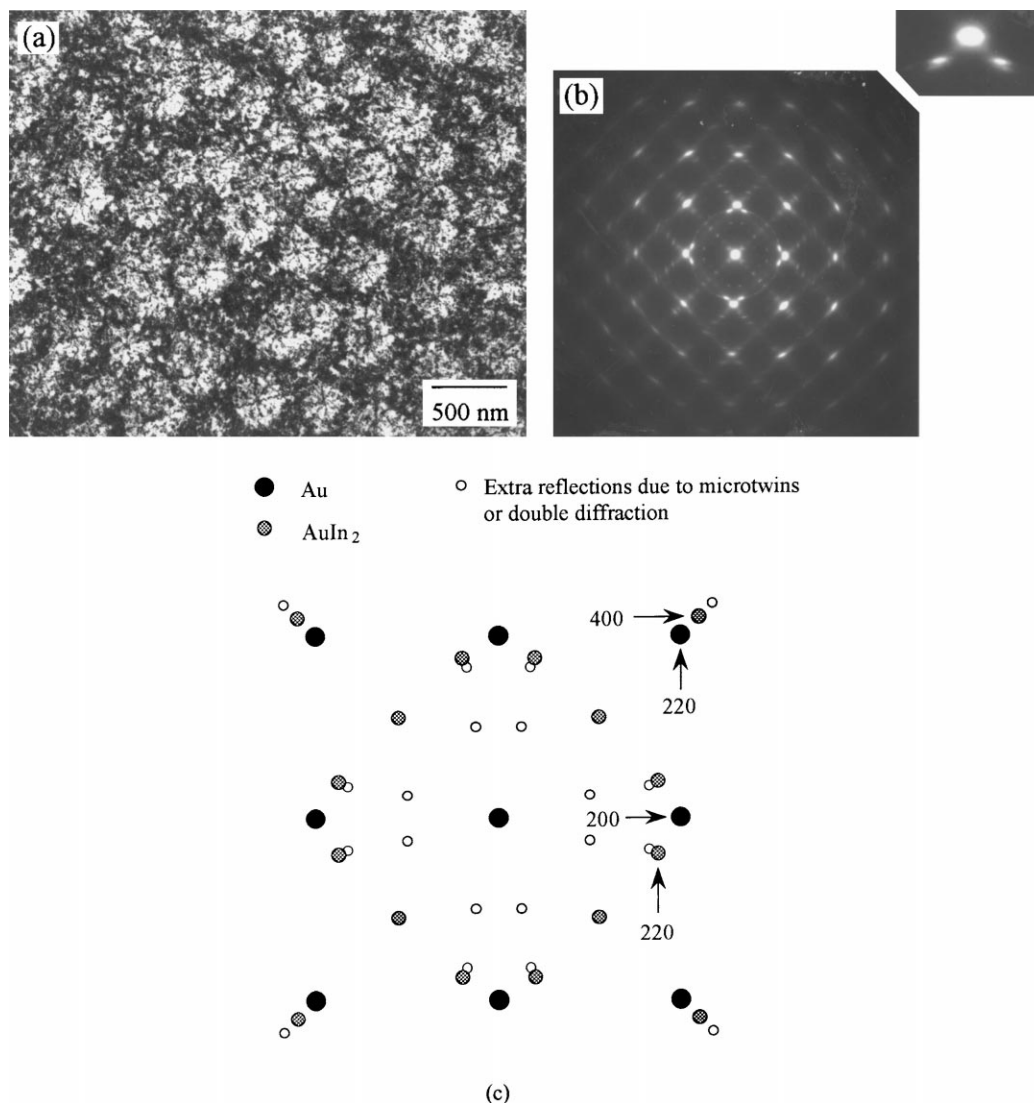


Fig. 5. TEM micrographs showing (a) the BF image, and (b) the SAD pattern of the In/Au bilayer deposited sequentially on the NaCl substrate. Inserted in the up-right corner of (b) is an enlargement of the reflection from Au microtwins. (c) A schematic indicating the origin of major reflections shown in (b).

portion of fractured segments. As a result of poor adhesion, the PET substrate delaminated from the joint during ultramicrotomy. The technique of ultramicrotomy has recently been utilized by Shieu and Lee [18] to probe the mechanical properties of a composite material. In general, a brittle material such as  $\text{AuIn}_2$  will shatter and form periodic cracks during ultramicrotomy. From the SAD pattern shown in Fig. 6(b) of an interfacial region, it is deduced that the equiaxial grains are pure In, and the fragments are identified to be  $\text{AuIn}_2$ . This result is consistent with that reported by Millares et al. [8], who found that the  $\text{AuIn}_2$  intermetallic represents the major phase in the reaction zone of a bulk Au–In diffusion couple.

Fig. 6(c) shows the cross-section microstructure of a region, near the center of the sandwiched Au/In/Au specimen, in the In foil about  $\sim 10 \mu\text{m}$  away from the In– $\text{AuIn}_2$

interface. For a single lap tensile test, the center region of the single lap specimen suffers the maximum shear stress. As a result of severe shear deformation, the polycrystalline In has transformed from a random orientation near the  $\text{AuIn}_2$  to a texture near the center of the single lap specimen. The existence of texture is illustrated both by the presence of a rectangular cell structure where high dislocation density can be readily seen in the BF image of Fig. 6(c), and by the pseudo single crystal SAD pattern of Fig. 6(d). The zone axis in the SAD pattern of Fig. 6(d) is close to the  $[001]$  direction of In which has a body-centered tetragonal crystal structure. The deformation texture consists of  $\{110\}$  planes oriented parallel to the substrate surface with  $\langle 111 \rangle$  directions, which is the primary slip system for a body-centered cubic metal, aligned in the maximum shear stress.

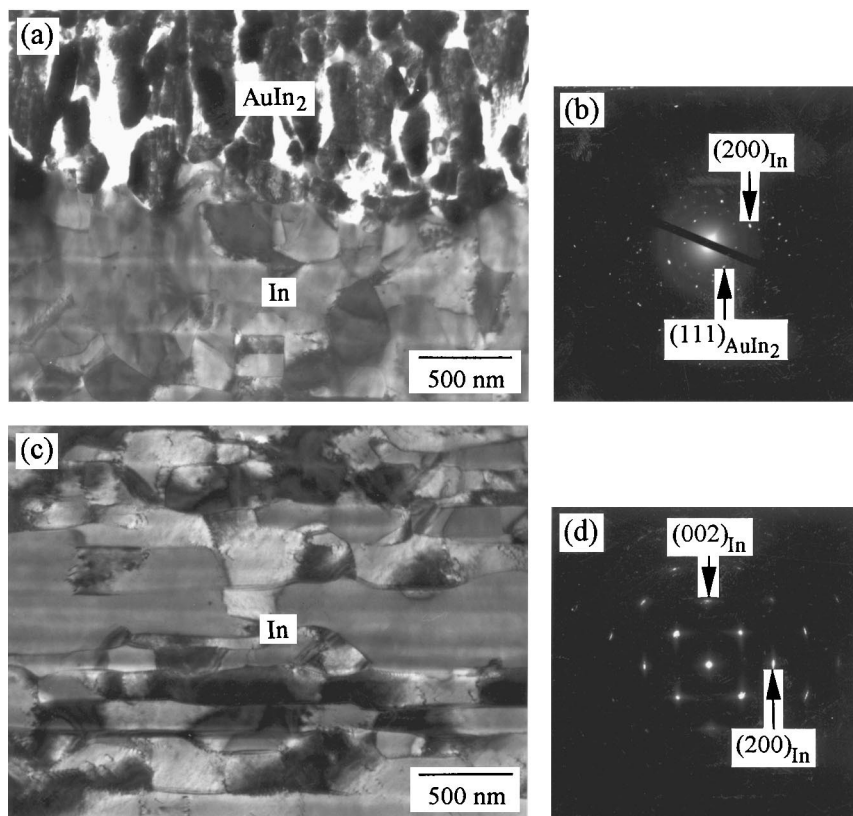


Fig. 6. (a) A cross-section TEM micrograph of the Au/In/Au microjoint after single lap tensile test. (b) The SAD pattern of an interfacial region in (a). (c) The microstructure of pure In about  $\sim 10\ \mu\text{m}$  away from the In–AuIn<sub>2</sub> interface. (d) The SAD pattern of the area in (c).

#### 4. Conclusions

It has been demonstrated that the growth mechanism of Au and In thin films deposited on the single crystals of NaCl substrate follows the Volmer–Weber mode. Unlike the In films that are polycrystalline, the Au films exhibit an epitaxial relationship,  $(001)_{\text{Au}}// (001)_{\text{NaCl}}$  and  $[001]_{\text{Au}}// [001]_{\text{NaCl}}$ , with the single crystals of NaCl substrate. When In was deposited onto the Au-coated NaCl, it was observed that the AuIn<sub>2</sub> phase is formed instantly, and the intermetallic grows layer by layer, i.e. it follows the Frank–van der Merwe mode as a result of the strong chemical interactions between Au and In. In addition, it is found that the AuIn<sub>2</sub> layer shows an epitaxial orientation to the underlayer Au substrate. By sandwiching an In foil between two Au films, it is observed that the major phase in the microjoint is the AuIn<sub>2</sub> intermetallic. From the cross-section TEM in which thin sections were prepared by ultramicrotomy, it can be deduced that the intermetallic AuIn<sub>2</sub> is brittle in nature.

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