

High Resolution Electron Microscopy of Low Temperature Silver- and Gold/Silver-Selenide, $\text{Au}_x\text{Ag}_{2-x}\text{Se}$ ($x=0-0.5$)

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HREM observations on thin films of Low Temperature Ag_2Se reveal the coexistence of various phases, while the presence of gold in thin $\text{Au}_x\text{Ag}_{2-x}\text{Se}$ films, prepared by reaction of epitaxial Au/Ag films with Se vapour, seems to stabilize the tetragonal cell only. Observed HREM and simulated images combined with optical diffraction and arguments on bond lengths allow the deduction of a structural model for this phase: Monoclinic pseudotetragonal, S.G. P2, $a=c=0.706$ nm, $b=0.498$ nm, $\beta=90^\circ$, $Z=4$, atomic positions: Se in 0, 0, 0; $1/2, 1/2, 0$; $1/2, 0, 1/2$; $0, 1/2, 1/2$; Ag in 0.84, 0, 0.34; 0.16, 0, 0.66; 0.3, 0.25, 0.25; 0.7, 0.25, 0.75; 0.36, 0.5, 0.64; 0.64, 0.5, 0.36; 0.2, 0.75, 0.25; 0.8, 0.75, 0.25.

KEY WORDS: Silver selenide/ Gold-Silver-Selenide/ Topotactic reaction/

INTRODUCTION

Silver selenide (Ag_2Se) undergoes a first order polymorphic transition at $133^\circ\text{C}^{1)}$. Above the transition temperature the high-temperature (HT) phase behaves as a metal and its structure, first determined by Ralphs²⁾, has also been described by other authors^{1,3)} as body-centred cubic with lattice parameter $a=0.498$ nm. Its unit cell contains two selenium atoms placed at the bcc lattice points and four silver atoms statistically distributed among the 42 interstitial sites.

Crystal structure data in the literature for the low-temperature (LT) semiconductor phases of Ag_2Se are contradictory. At temperatures below the transition point, the compound has been described as cubic, tetragonal, orthorhombic, triclinic and sometimes as monoclinic (Table 1) for specimens prepared using different methods and conditions. Wiegers¹³⁾ has determined a LT- Ag_2Se structure by X-ray powder methods and found an orthorhombic cell with space group $\text{P2}_12_12_1$, which is completely different from the structure described by Pinsker et al.⁸⁾. It seems that other LT- Ag_2Se phases are only stable in thin films. Y. Saito et al.¹⁸⁾ investigated Ag_2Se films and found that tetragonal, orthorhombic and triclinic modifications exist as distinct LT phases. The crystal structures of the orthorhombic and triclinic phases of Ag_2Se have been determined from observed structure images and their computer simulated images by C. Kaito et al.²¹⁾. They found space group P222 for the orthorhombic and P1 for the triclinic cell, P422 is proposed for the tetragonal form.

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Table 1. Literature data for LT-Ag₂Se phases (not complete)

Symmetry	Lattice constants	Investigation method	Ref.
Tetragonal	$a=b=0.706$ nm $c=0.498$ nm	Electron diffraction as $f(T)$	[3]
Tetragonal, after heating and cooling cycle	$a=b=0.498$ nm $c=0.478$ nm		
Tetragonal	$a=b=0.706$ nm $c=0.498$ nm	X-ray diffraction	[4]
Not tetragonal	—	X-ray diffraction	[5]
Orthorhombic	$a=0.434$ nm $b=0.711$ nm $c=0.779$ nm	X-ray diffraction	[6]
Orthorhombic	$a=0.705$ nm $b=0.433$ nm $c=0.782$ nm	Electron diffraction	[7]
Orthorhombic P22 ₁	$a=0.705$ nm $b=0.433$ nm $c=0.785$ nm	Electron diffraction	[8]
Orthorhombic	$a=0.434$ nm $b=0.707$ nm $c=0.775$ nm	X-ray diffraction	[9]
Orthorhombic	$a=0.705$ nm $b=0.432$ nm $c=0.782$ nm	Electron diffraction	[10]
Orthorhombic	$a=0.705$ nm $b=0.783$ nm $c=0.433$ nm	Electron diffraction as $f(T)$	[11]
Orthorhombic	$a=0.705$ nm $b=0.425$ nm $c=0.806$ nm	Electron diffraction	[12]
Orthorhombic P2 ₁ 2 ₁ 2 ₁	$a=0.433$ nm $b=0.706$ nm $c=0.776$ nm	X-ray diffraction	[13]
Tetragonal (metastable)	$a=b=0.706$ nm $c=0.498$ nm	Electron diffraction as $f(T)$	[14]
Orthorhombic	$a=0.705$ nm $b=0.785$ nm $c=0.433$ nm		
Orthorhombic	$a=0.705$ nm $b=0.785$ nm $c=0.433$ nm	Electron diffraction	[15]
Monoclinic	$a=0.423$ nm	Electron diffraction	

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	$a=0.691 \text{ nm}$ $c=0.787 \text{ nm}$ $\beta=99^\circ 35'$		
Orthorhombic	$a=0.434 \text{ nm}$ $b=0.706 \text{ nm}$ $c=0.776 \text{ nm}$	Electron diffraction as $f(T)$	[16]
Pseudo orthorh., triclinic	$a=0.70 \text{ nm}$ $b=0.78 \text{ nm}$ $c=0.43 \text{ nm}$ $\alpha=92^\circ$ $\beta=91.5^\circ$ $\gamma=92^\circ$	Electron diffraction	[1]
Pseudo orthorh., tric.	Lattice parameters as in [1]	Electron diffraction	[17]
Cubic fcc, metastable Orthorhombic	$a=0.565 \text{ nm}$ $a=0.434 \text{ nm}$ $b=0.706 \text{ nm}$ $c=0.776 \text{ nm}$	Electron diffraction	[18]
Tetragonal (with excess Ag) Orthorhombic	$a=b=0.706 \text{ nm}$ $c=0.498 \text{ nm}$ $a=0.706 \text{ nm}$ $b=0.780 \text{ nm}$ $c=0.434 \text{ nm}$	Electron diffraction	[19]
Triclinic	$a=0.699 \text{ nm}$ $b=0.779 \text{ nm}$ $c=0.430 \text{ nm}$ $\alpha=92^\circ$ $\beta=91.5^\circ$ $\gamma=92^\circ$		
Monoclinic ($\geq 45^\circ\text{C}$)	$a=0.691 \text{ nm}$ $b=0.787 \text{ nm}$ $c=0.423 \text{ nm}$ $\alpha=99.58^\circ$		
Orthorhombic, triclinic Tetragonal, P422	Lattice param. as [21] $a=b=0.706 \text{ nm}$ $c=0.498 \text{ nm}$	Electron diffraction Not indicated	[20]
Orthorhombic, P222	$a=0.706 \text{ nm}$ $b=0.780 \text{ nm}$ $c=0.434 \text{ nm}$	Electron diffraction HREM, computer sim.	[21]
Triclinic, P1	$a=0.70 \text{ nm}$ $b=0.78 \text{ nm}$ $c=0.43 \text{ nm}$ $\alpha=92^\circ$ $\beta=91.5^\circ$ $\gamma=92^\circ$		

The only known compound in the system Au-Ag-Se is Ag_3AuSe_2 , a mineral called "fischesserite", isostructural to Ag_3AuTe_2 (petzite), space group $I4_132^{22}$ with lattice parameter $a=0.997$ nm. Tavernier et al.²⁴⁾ performed differential thermo-analytical investigations on silver-gold(I)-chalcogenides. They found that silver in Ag_2Se can be substituted by gold in aqueous solution of $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ up to 25 at% leading to the composition AuAg_3Se_2 , determined earlier by Messien et al.²³⁾.

In our investigations we produced thin epitaxially grown silver and mixed silver/gold films on (100) cleaved KCl faces and studied the structural changes after selenation.

EXPERIMENTAL

Thin films of $\text{Au}_x\text{Ag}_{2-x}\text{Se}$ were prepared by vacuum deposition of the compo-

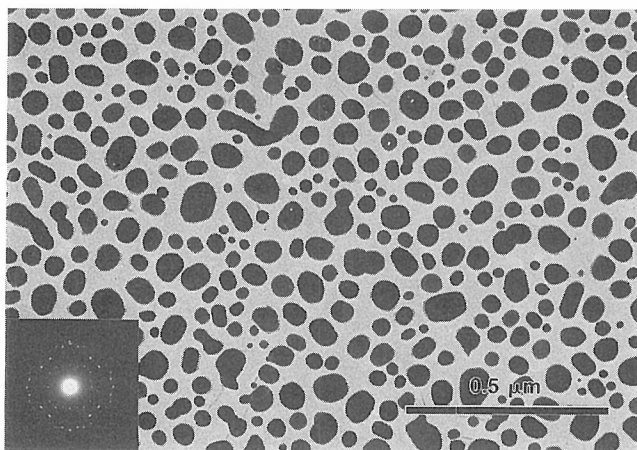


Fig. 1. Selenized 15 nm thick Ag-film (Ag_2Se) deposited onto (100) cleavage face of KCl at a substrate temperature of 300°C. Inset: SAED pattern. Lattice orientation: $[010]_{\text{tet.}} // [001]_{\text{Ag}}$.

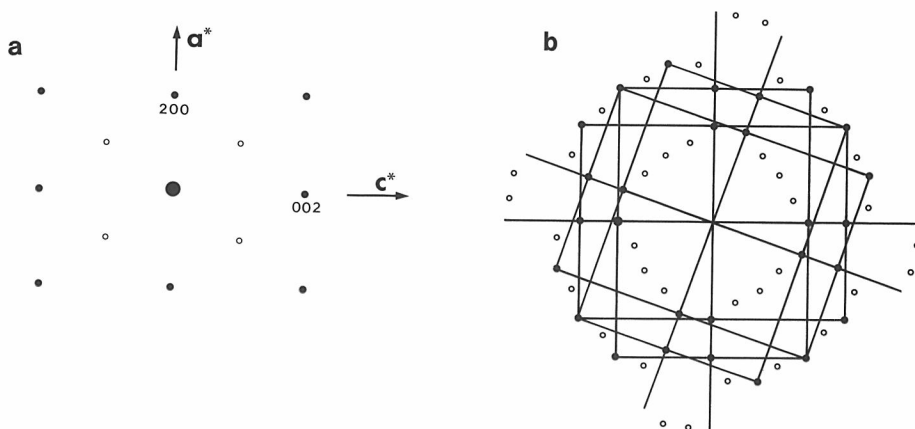


Fig. 2. a) Basic diffraction pattern of the tetragonal Ag_2Se -phase. b) Superposition of four orientations; rotations by 19.5, 90 and 109.5°.

nents on KCl crystals, which were (001)-cleaved in air and then immediately placed in a chamber to be evacuated down to $<6.5 \cdot 10^{-5}$ Pa. Silver or silver/gold was deposited onto the preheated KCl surface (300°C for four hours) from a tungsten boat at a deposition rate of about 1.2–1.5 nm/min. Rate and film thickness were measured with an oscillating quartz crystal microbalance. Selenium was evaporated onto the Ag- or Au/Ag-films immediately after the substrate temperature had reached $210-230^\circ\text{C}$ (measured with a constantan-Ni thermocouple) or after cooling to room temperature (to take out samples) and heating up again to 200°C at a deposition rate between 1.2–20 nm/min. Films were annealed at the same temperature for 15 min (annealing at higher temperatures leads to decomposition) and then cooled to room temperature. These layers were covered with a 10 nm thick carbon layer to stabilize the small crystallites, wet stripped in bidis-

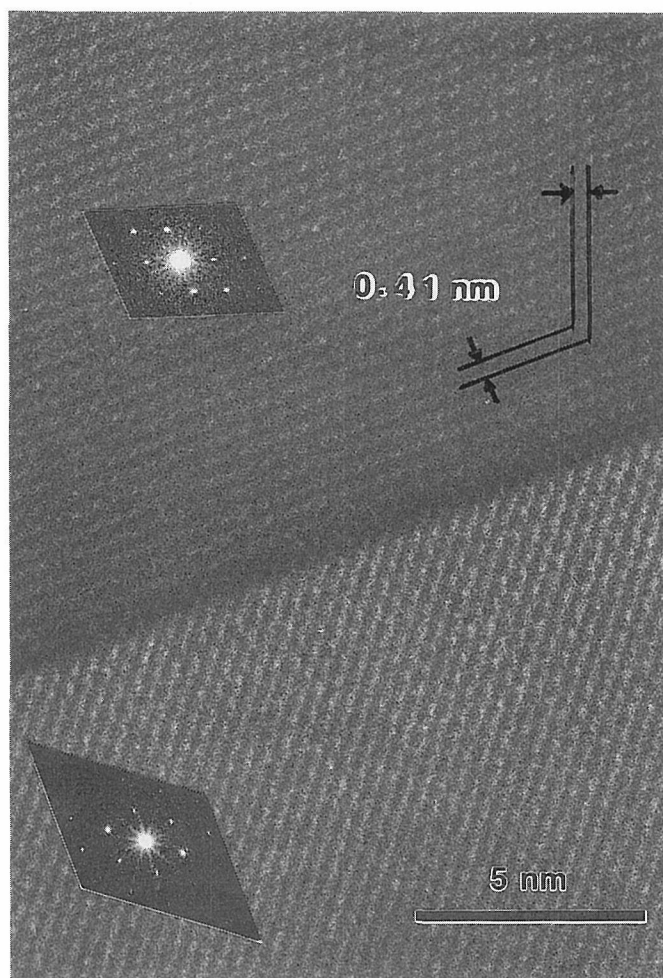


Fig. 3. HREM image of a twinned tetragonal Ag_2Se crystal, $[010]$ zone axis. Fringes with 0.41 nm correspond to the (101) planes. Inset; Optical diffraction patterns.

tilled water and collected on holey carbon films on copper specimen grids. The composition of the Au/Ag-layers is not identical with the weighted proportion of the metals as shown by quantitative electron microprobe analysis (ARL electron microprobe). Electron microscopic observations were performed within a JEOL 200CX electron microscope operating at 200 kV ($c_s=1.2$ mm) or within a Hitachi HU-125S EM operating at 75 kV for low magnification images and selected area electron diffraction (SAED). Simulated images and electron diffraction patterns for various trial models were calculated by the EMS programs²⁵). Optical diffraction patterns were obtained with a laser diffractometer, built according to Ref. 26, 27.

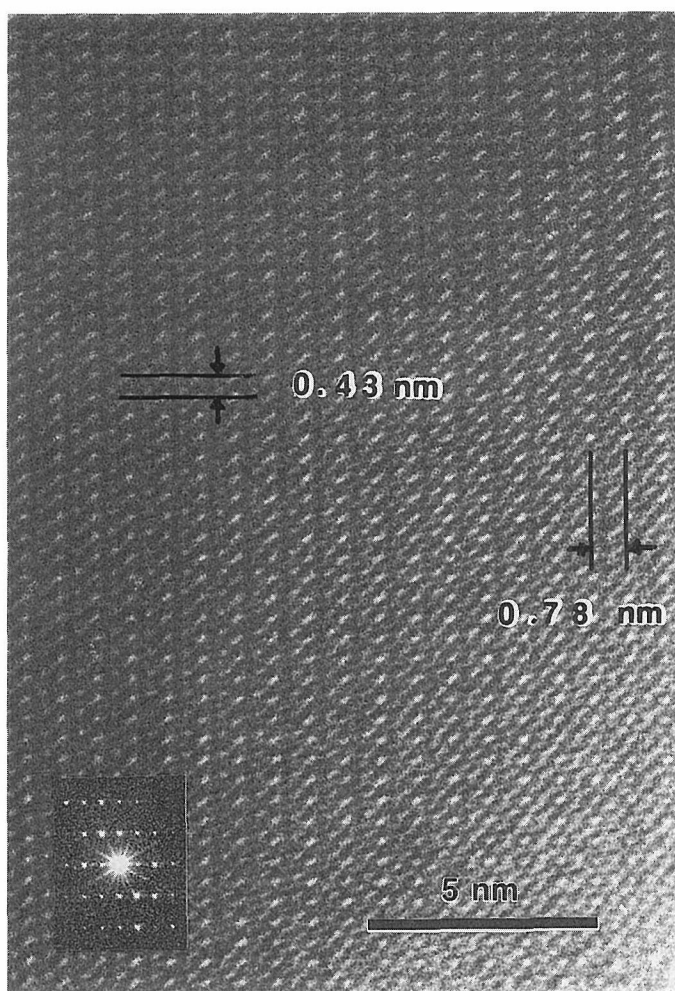


Fig. 4. HREM image of an orthorhombic Ag_3Se crystal with the $[100]$ direction parallel to the film normal. Fringes with 0.78 and 0.43 nm correspond to the (010) and (001) planes. Inset: Optical diffraction pattern.

RESULT AND DISCUSSION

Thin Films of Pure Ag_2Se

Epitaxially grown thin silver films were obtained in two different ways: evaporation of a 2 nm Ag-layer at T_{KCl} : 300°C for prenucleation followed by a second evaporation of silver (10–13 nm) either at T_{KCl} : 300°C or after cooling the substrate to room temperature. Selenation of these silver films at T_{KCl} : 230°C leads to Ag_2Se -layers whose SAED patterns indicate either a mixture of triclinic, orthorhombic and tetragonal phases or show large areas with d-spacings corresponding to the tetragonal cell (Fig. 1).³⁾ Lattice orientation: $[010]_{\text{tetr.}} // [001]_{\text{Ag}}$. The continuous silver film has broken up into islands, but is still oriented. The

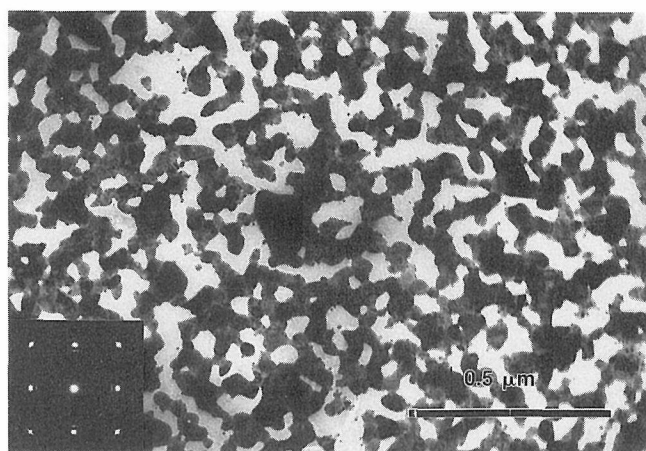


Fig. 5. Epitaxially grown, continuous Au/Ag-film ($x=0.5$), 15 nm thick, T_{KCl} : 300°C .

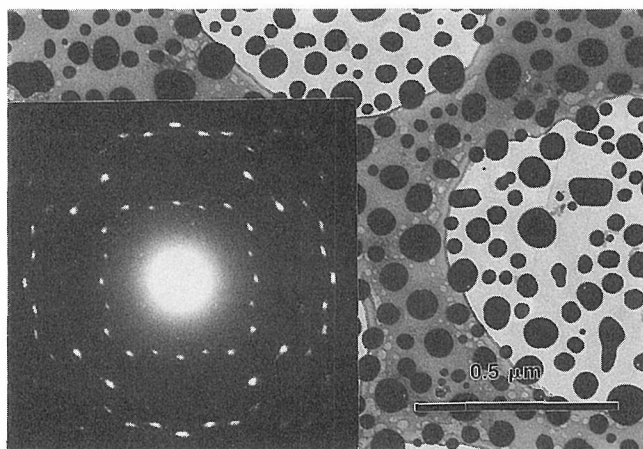


Fig. 6. Au/Ag-film (as in Fig. 5) after reaction with Se vapour at T_{KCl} : 200°C , annealing at the same temperature for 1 hr and cooling. The film has broken up into islands, but is still oriented. Inset: SAED pattern.

basic electron diffraction pattern consists of rectangular arrays of spots with edges in the ratio of $1:\sqrt{2}$. The additional spots are due to rotations of the basic pattern by 19.5° , 90° and 109.5° as a consequence of corresponding 90° rotations of crystallites and twinning on (101) planes (Fig. 2), as discussed by Dhere et al.¹²⁾ for HT-Ag₂Se. All HREM images observed belong to the $[100]$ zone axis of twinned tetragonal Ag₂Se crystals (Fig. 3), as proved by optical diffraction patterns. Among the tetragonal crystals one could find occasionally singular orthorhombic particles, which do however not contribute to the overall SAED pattern (Fig. 4).

Thin Films of Au_xAg_{2-x}Se ($x=0.1-0.5$)

Based on our results on the preparation of thin epitaxially grown mixed Ag/

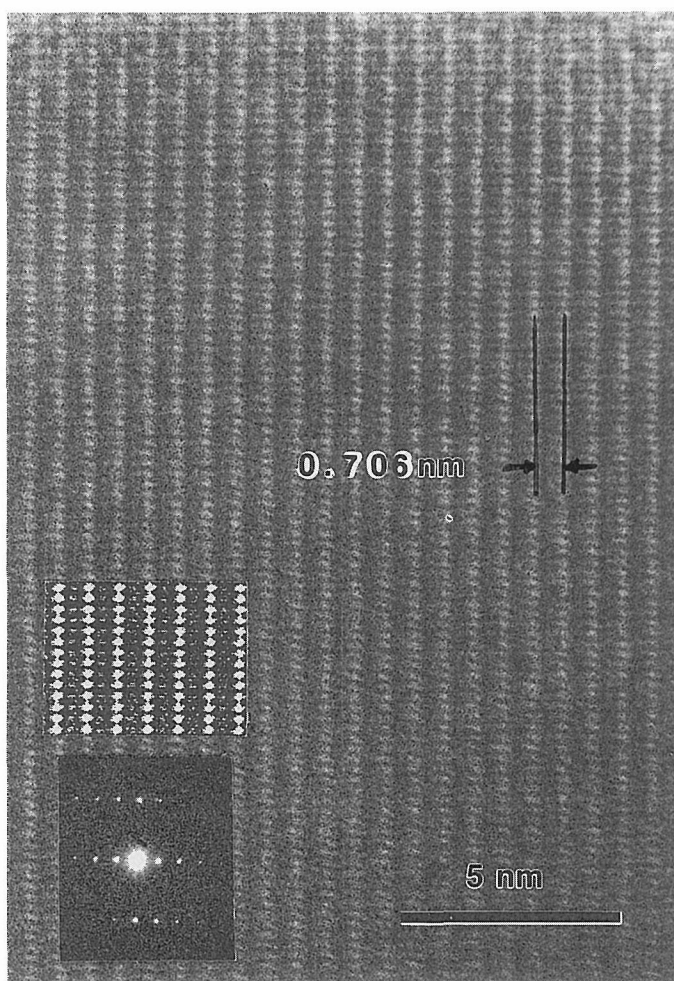


Fig. 7. Pseudotetragonal Au_xAg_{2-x}Se ($x=0.5$), $[100]$ zone axis. Fringes with 0.706 nm correspond to (001) planes. Insets: Optical diffraction pattern and simulated image (200 kV, Defocus: -72 nm, Thickness: 14 nm).

Au-layers²⁸⁾, we have studied the reaction of such films with selenium vapour. Fig. 5 shows a low magnification electron micrograph and a corresponding selected area electron diffraction (SAED) pattern of a mixed Ag/Au-layer (15 nm thick), grown on (100) KCl faces at a substrate temperature of 300°C with parallel lattice orientation relative to the silver. The content of gold in the continuous film lies between 15 and 20 at %, as revealed by quantitative electron microprobe analysis for thicker layers (25 nm). After reaction with Se vapour at T_{KCl} : 200°C (until the microbalance with its quartz crystal held at room temperature indicated a thickness of 15 nm for fully selenized samples), the film has broken up into islands as illustrated by Fig. 6. Its SAED pattern shows d-spacings corresponding to the tetragonal cell with additional spots due to rotations and twinning (see Fig. 2), a

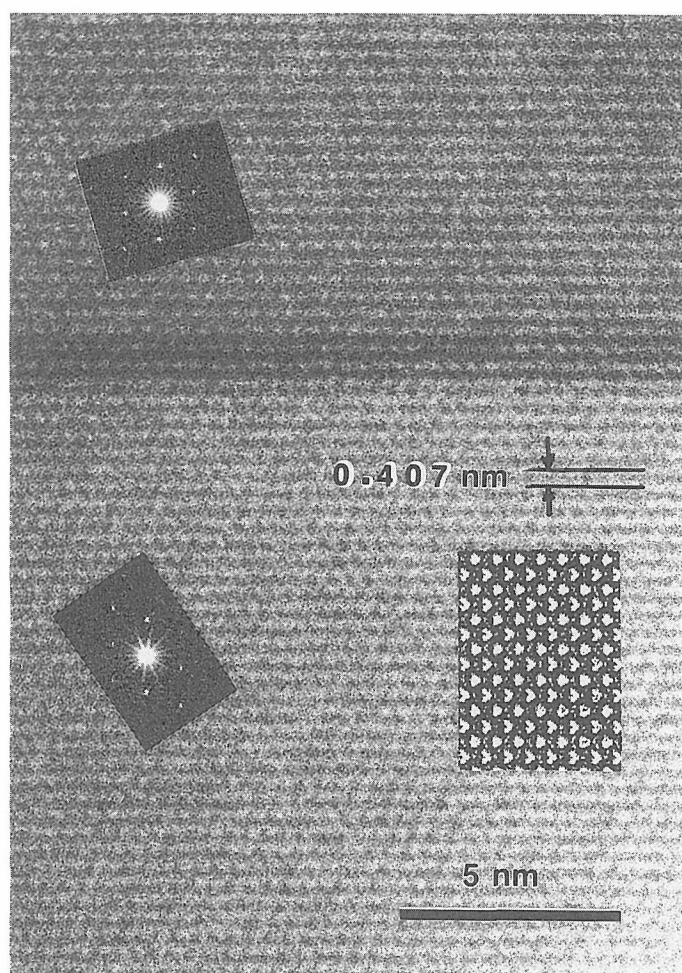


Fig. 3. Twinned pseudotetragonal $\text{Au}_x\text{Ag}_{2-x}\text{Se}$ crystal, $[001]$ zone axis. Fringes with 0.407 nm correspond to (110) planes. Insets: Optical diffraction pattern and simulated image (200 kV, Defocus: -77 nm, Thickness: 14 nm).

consequence of the deposition temperature being higher than the transition point; the bcc HT-Ag₂Se phase twins on (211) planes^{1,16)} and then induces twinning on (101) planes in the tetragonal phase at room temperature. This behaviour is different from that observed for triclinic pure Ag₂Se.²⁹⁾

Variation of the Au content (5–25 at %) reproducibly yields electron diffraction patterns with tetragonal symmetry as shown in Fig. 4 and 5 over the entire samples. In high resolution electron microscopic observations of these layers, three different types of crystallites could be observed, illustrated by Fig. 7–9 (unit cell of²¹⁾). An example of the frequently observed crystal defects is shown in Fig. 10. Shiojiri et al.²⁰⁾ proposed as space group P422 for the tetragonal

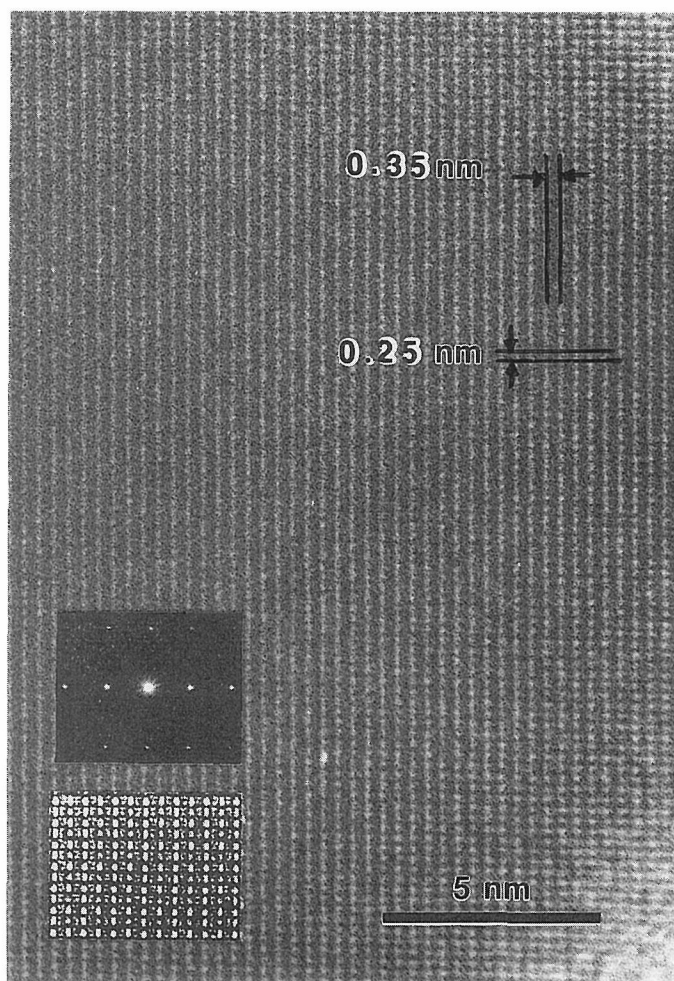


Fig. 9. Pseudotetragonal Au_xAg_{2-x}Se crystal, [001] zone axis. Fringes with 0.353 and 0.25 nm correspond to (200) and (020) planes. Insets: Optical diffraction pattern and simulated image (200 kV, Defocus: -92 nm, Thickness: 14 nm).

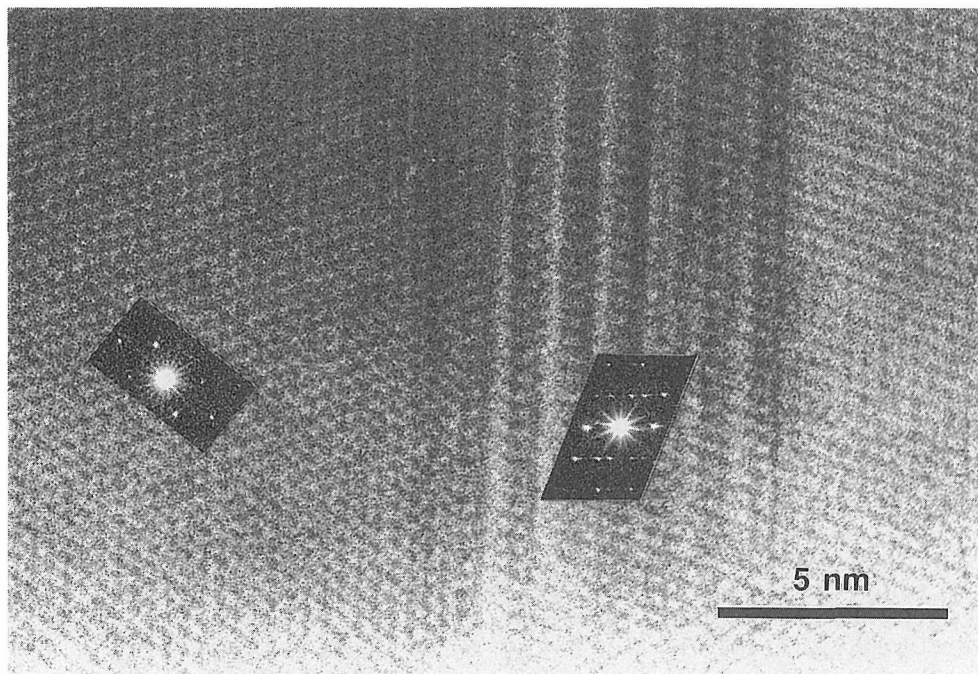


Fig. 10. Example for the frequently observed crystal defects in $\text{Au}_x\text{Ag}_{2-x}\text{Se}$ crystals, which are not yet fully understood. Insets: Optical diffraction patterns.

LT- Ag_2Se , but simulated images and calculated electron diffraction patterns using the coordinates given for Se and Ag do not explain our electron micrographs. Calculations on various trial models, taking into consideration reasonable bond distances, only lead to a satisfactory agreement for a pseudotetragonal unit cell with the monoclinic space group P2, with $a=c=0.706$ nm, $b=0.498$ nm, $\beta=90^\circ$, $Z=4$. The Se atoms are placed in face centering positions of the pseudotetragonal lattice and the Ag atoms have the following coordinates: 0.84, 0, 0.34; 0.16, 0, 0.66; 0.3, 0.25, 0.25; 0.7, 0.25, 0.75; 0.36, 0.5, 0.64; 0.64, 0.5, 0.36; 0.2, 0.75, 0.25; 0.8, 0.75, 0.25.

The Ag-Ag distances in thin Ag_2Se films of space group $\text{P}222_1$ determined by Pinsker et al.⁸⁾ are short, ranging from 0.261 to 0.282 nm (in metallic silver: 0.289 nm). This structure contains Ag-Se-Ag-Se chains with short Ag-Se distances of 0.254 nm. For the structure described by Wiegers¹³⁾ in space group $\text{P}2_12_12_1$ the shortest Ag-Ag distance is 0.293 nm, the shortest Ag-Se bond 0.262 nm. The model proposed by Shiojiri et al.²⁰⁾ (tetragonal, space group $\text{P}422$) contains four extremely short Ag-Ag contacts of 0.255 nm. The shortest Ag-Ag distance in our model is 0.261 nm similar to Pinsker et al.⁸⁾, the other Ag-Ag distances range between 0.28 and 0.329 nm. Assuming a minimum Ag-Se contact of 0.262 nm, we performed our model calculations by distributing the Ag atoms into the largest interstices (42 possibilities for Ag atoms).

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