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An X-ray diffraction and electron spectroscopic study of metallic glass $In_{20}Te_{80}$

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Results of X-ray diffraction and X-ray photoelectron spectroscopy investigations on the crystallization behaviour of an amorphous $In_{20}Te_{80}$ system and the effects of crystallization on the electronic core levels of In and Te atoms are presented. During controlled heat treatments three crystalline phases, Te, α-In_2Te_3, and In_2Te_5-I, were observed in this system. In addition, a few splat-cooled samples were found to exhibit a new metastable crystalline phase. Photoelectron measurements revealed that the Te 3d and 4d core levels of amorphous $In_{20}Te_{80}$ were shifted downwards in energy from their characteristic values of pure Te metal. The In 3d and 4d levels experienced large energy shifts due to alloying, but remained unaffected by heating at temperatures below 520 K.

1. Introduction

Tellurium alloys were among the first to be obtained in the amorphous state by rapid quenching from liquids [1]. These semiconducting glasses exhibit a number of interesting properties, e.g., electrical transport properties [2]. The present paper deals with indium–tellurium metallic glass containing 20 at% In prepared by a splat-cooling technique. The aim of this work was to study the crystallization behaviour, due to annealing, and the effects of crystallization on the core level electronic structures of In and Te atoms. The experimental methods employed in these measurements were X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experimental procedure

The alloys of pure metals (Te 99.999% and In 99.995%) were melted under an argon atmosphere by induction melting. The molten ingot was first mixed using eddy currents and then the ingot was heated at 570 K for 16 h under an atmosphere of pure argon to ensure the homogeneity of the alloy composition. The surface layer of the ingot was removed mechanically and charges of 50 to 100 mg were made for splat-cooling. The splat-cooling was carried out using the piston–anvil apparatus [3] under a high-purity argon atmosphere. The samples obtained were circular in shape having a diameter of about 1.5 cm and a thickness of less than 70 μm.

For diffraction measurements, heat treatment of the splat-cooled foils was carried out using a modified Anton Paar high-temperature attachment for the diffractometer. The reflected Cu$K\alpha$ and Mo$K\alpha$ radiations were investigated using a Si (Li) semiconductor detector (FWHM = 175 eV/5.9 keV) connected to a single channel pulse height analyser by which the $K\beta$ reflections were eliminated.

The XPS measurements were made using a VG Scientific ADES-400 multitechnique electron spectrometer. The spectra were measured at room temperature before and after heating the samples *in situ* to 450 and 520 K. Heating at higher temperatures was avoided because it would cause a

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remarkable enrichment of In in the surface region, owing to evaporation of Te.

3. Results and discussion

3.1. XRD analysis

During controlled annealing treatments, three crystalline phases were observed in the originally amorphous alloy. These phases were Te (hexagonal, $a = 0.445$ nm, $c = 0.593$ nm), α-In_2Te_3 (fcc, $a = 0.616$ nm), and In_2Te_5–I (monoclinic, $a = 0.439$ nm, $b = 1.639$ nm, $c = 1.352$ nm, $\beta = 91.65°$). In addition, some specimens exhibited a hitherto unknown phase, denoted as θ. The θ-phase was tetragonal with the lattice parameters equal to $a = 1.088$ nm and $c = 0.734$ nm.

It was found that crystallization occurred during isochronal heating at 420 K by a primary precipitation of pure Te. At higher temperatures a polymorphic crystallization of α-In_2Te_3 occurred. This phase was unstable and decomposed into stable Te and In_2Te_5–I crystalline phases.

The above-mentioned crystalline behaviour is shown in Fig. 1 by a set of XRD charts. The crystallization temperatures were determined by raising the temperature in steps of 10 K and annealing the samples at each temperature for 1 h. They were found to be 420, 550 and 670 K for Te, α-In_2Te_3 and In_2Te_5–I, respectively. The relative abundance of these phases were also studied and the results are shown in Fig. 2. The growth of the Te phase appears to cease as α-In_2Te_3 starts to form, while above 670 K, α-In_2Te_3 decomposes and In_2Te_5–I starts to form. There is a certain probability that an amount of Te has evaporated in this situation from the initial composition.

3.2. XPS analysis

The binding energies of the $3d_{5/2}$ and 4d core levels of In and Te atoms were measured by the XPS method before and after annealing. The binding energies obtained are listed in Table I. A survey of the table reveals that there exist two separate Te $3d_{5/2}$ structures in each spectrum. The low-energy component at 573.1 eV for the amorphous alloy originates from Te in the bulk of the alloy. It is located 0.2 to 0.3 eV lower than the $3d_{5/2}$ level in crystalline pure Te according to our earlier measurements [4]. The high-energy component at 576.6 eV remains constant in energy when heating. This component originates from the oxidized surface and would be completely removable by argon-ion bombarding. However, we did not bombard the surfaces of the present samples since our earlier studies on ion-bombarded In–Te samples indicated the presence of serious surface damage which shifted the XPS lines. It should be noted that the Te $4d_{5/2,3/2}$ levels in the oxide layer are also shifted downwards in energy by several eVs. Therefore, 4d of the oxide does not interfere with 4d of the bulk. Unfortunately, the In $3d_{5/2}$ and 4d levels of the oxide and the bulk are non-separable. This fact somewhat complicates a study of the chemical surroundings of In atoms.

The annealing reduces the binding energies of the Te 3d and 4d levels by 0.1 to 0.2 eV. The binding energy of $3d_{5/2}$ obtained after heating the samples at 520 K coincides with the energy of $3d_{5/2}$ in crystalline Te and shows that a considerable amount of Te must have precipitated during heating. This observation is in qualitative agreement with the XRD data. It is interesting to note that the 4d levels of the alloy lie somewhat deeper in energy than those of crystalline Te. This fact implies that the measured 4d signal is probably composed of several closely spaced energy levels derived from pure Te and $In_{20}Te_{80}$.

The In $3d_{5/2}$ and 4d levels are located well below (> 1 eV) the corresponding levels of crystalline indium. In general, a difference between corresponding energy levels in crystalline and amorphous states of any alloy is expected to be very small.

TABLE I The binding energies of 3d and 4d photoelectrons for amorphous In–Te metal before and after heat treatments. The energies are given within the estimated error limits of ± 0.10 eV relative to the $3d_{5/2}$ level of a vacuum-deposited Ag film for which the binding energy was taken to be 368.20 eV

Core level	Binding energy (eV)		
	As-received no heating	After heating at 470 K	After heating at 520 K
Te $3d_{5/2}$	573.10	573.00	572.90*†
Te $4d_{5/2}$	40.80	40.70	40.70
Te $4d_{3/2}$	42.20	42.10	42.10
In $3d_{5/2}$	445.10	445.00	444.90‡
In 4d	18.70	18.60	18.60§

*For a pure Te film the binding energies are 572.85 ± 0.15, 40.46 ± 0.10 and 41.96 ± 0.10 eV for $3d_{5/2}$, $4d_{5/2}$ and $4d_{3/2}$, respectively; see Pessa *et al.* [4].

†The binding energy of Te $3d_{5/2}$ in the oxidized surface of In–Te was found to be 576.6 eV ± 0.2 eV independent of the heat treatment.

‡For a pure In film the binding energies are 443.84 ± 0.15, 16.76 ± 0.10 and 17.64 ± 0.10 eV for $3d_{5/2}$, $4d_{5/2}$ and $4d_{3/2}$, respectively [4].

§This is the average value of $4d_{5/2}$ and $4d_{3/2}$.

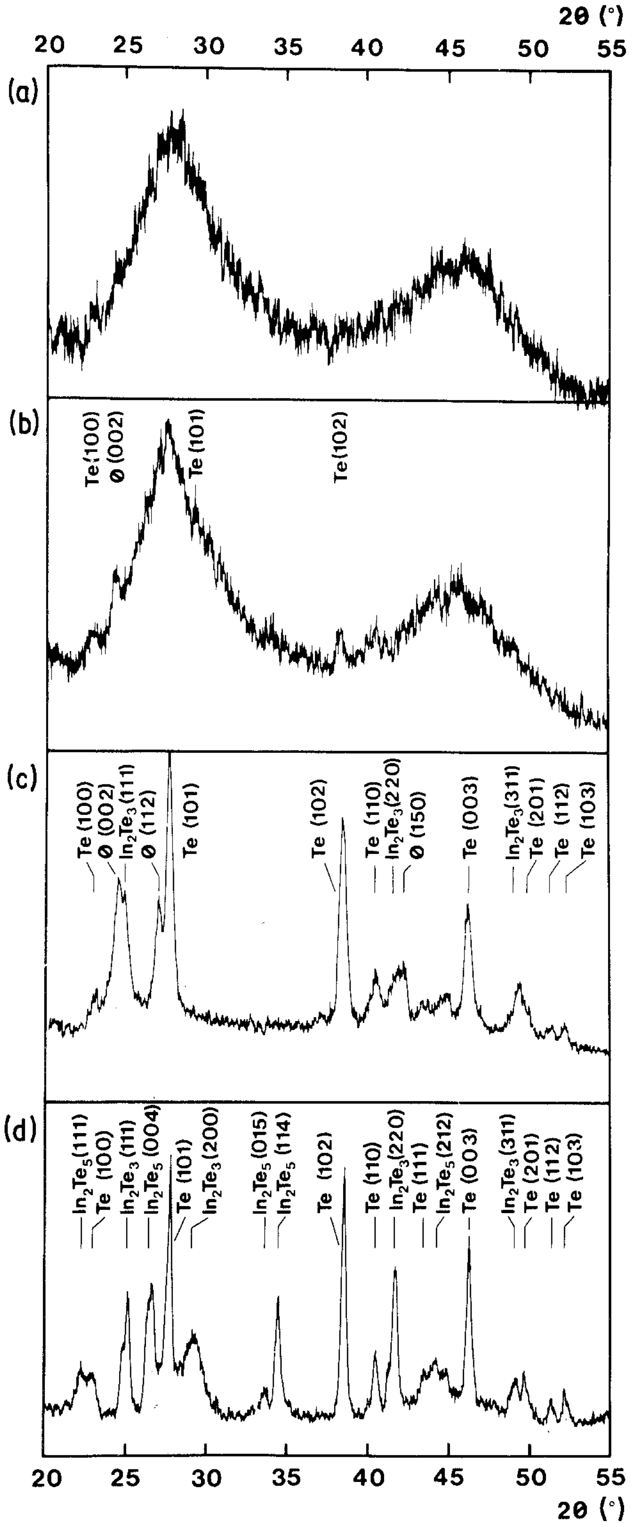

Figure 1 Diffraction patterns of $In_{20}Te_{80}$ alloy in different stages: (a) glass (room temperature); (b) crystallization of Te has started, also the first reflection of the θ-phase can be observed (430 K); (c) separation of α-In_2Te_3 starts (570 K); (d) after complete crystallization (670 K).

Therefore, the observed shifts of 1 eV in $In_{20}Te_{80}$ must be associated with alloying effects rather than amorphism. The absence of In 3d and 4d signals at 443.8 and 16.7 to 17.6 eV, typical of crystalline pure In metal, reveals that there exists no measurable precipitation of In. The shifts of 0.1 to 0.2 eV of 3d and 4d observed for the heated samples can be interpreted as due to a partial

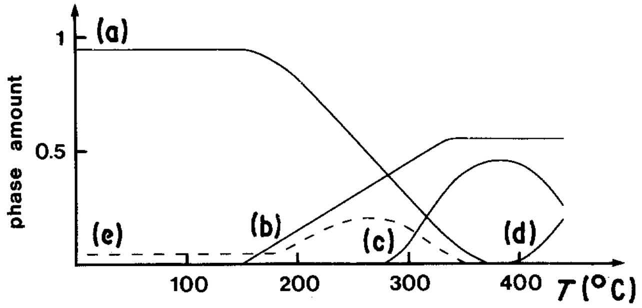

Figure 2 Relative abundance of the different phases of $In_{20}Te_{80}$ as a function of annealing temperature. (a) Amorphous; (b) crystalline Te; (c) α-In_2Te_3; (d) In_2Te_5–I; (e) θ-phase.

removal of oxygen from the surface by the heat treatment, as deduced from a decrease in intensity of the oxygen in the XPS line. Because the In signals of the bulk overlap with those of the oxidized surface, an enhancement of the bulk contribution shifts the centre of the composite line towards the 3d and 4d binding energies of amorphous $In_{20}Te_{80}$. In other words no appreciable effect of heating on the In core level structure can be found. This result is expected on the basis of the XRD data obtained for the temperature regime below 520 K.

Finally, it should be noted that small amounts of oxygen and carbon as impurities in the surface made it impossible to study the valence band structures of the samples by using the XPS technique. Therefore, experiments on preparing clean amorphous In–Te film in an ultra-high vacuum of the XPS spectrometer are under way in our laboratories.

4. Conclusion

A combined XRD and XPS study on the crystallization behaviour of amorphous $In_{20}Te_{80}$ metal and the 3d and 4d electronic core level features of In and Te atoms as a function of annealing temperature has been reported. The results show that this combination of techniques is useful when probing the crystal and electronic structures of alloy systems.

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References

1. H. L. LUO and P. DUWEZ, *Appl. Phys. Lett.* 2 (1963) 21.
2. S. K. HSIUNG and R. WANG, *J. Appl. Phys.* 49 (1978) 280.
3. E. LAINE, E. HEIKKILÄ and I. LÄHTEENMÄKI, *Rev. Sci. Instrum.* 42 (1971) 1724.
4. M. PESSA, A. VUORISTO, M. VULLI, S. AKSELA, J. VÄYRYNEN, T. RANTALA and H. AKSELA, *Phys. Rev. B* 20 (1979) 3115.

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