

07.2-8 SEVERAL LONG-PERIOD CRYSTAL LATTICES FORMED BY SOLID-STATE REACTION IN Bi-Mn DOUBLE LAYER FILMS. By K. Yoshida, Y. Taniguchi and T. Yamada, Department of Applied Physics, Faculty of Engineering, Kobe University, Rokkadal, Nada, Kobe 657, Japan.

It has long been a well known fact that the ferromagnetic MnBi phase is the only alloy phase which is described in the Bi-Mn phase diagram. However, it became clear that a few other phases exist in this binary system, especially when they are prepared by vacuum deposition (Yoshida et al., *Acta Metall.*, 1986, 34, 969). It was also found that two or more novel long-period crystal lattices form by solid state reaction at the interface of Bi and Mn double layer films (Yoshida et al., *Proc. Xth Intern. Congr. of Electron Microscopy*, Kyoto, 1986, p. 1386). In this presentation, these long-period crystal lattices, derived from electron diffraction patterns, and their lattice images by high resolution electron microscopy will be shown.

The composite double layer films consist of an Mn layer of about 200 Å on a Bi layer of 300 Å, which were vacuum deposited onto carbon film in succession in a vacuum of  $10^{-6}$  Torr. They were then annealed in the same vacuum at a temperature a little below 271°C, the melting point of Bi, for a period of time ranging 5 to 100 hr. The observations were performed with a high resolution electron microscope, JEM 200-CX.

When observed in conventional bright-field images, underlying Bi crystals are extended wide and show well defined grain boundaries. The Mn layer, which had extended over the Bi surface, shows coagulation into small lumps 100 to 200 Å in diameter. At the same time, many of these Mn lumps show parallel straight fringes even when the smallest objective aperture, corresponding to 6 Å in radius, is used. Their selected area diffraction patterns show a few faint, but clear, spots very near the incident beam, showing that very long periods are developed in the specimens. At first, these fringes were suspected to be moiré fringes due to double diffraction of the electrons. However, they are too straight and too well defined in many cases and the lumps give systematic single crystalline net patterns in electron diffraction.

Many such electron diffraction patterns were taken and we tried to construct a three-dimensional reciprocal lattice from them. For some specimens involving large lumps, the specimen tilt stage was used to get different planar sections of the reciprocal lattice. The reciprocal lattices were then transformed into the real space to derive the following three crystal lattices:

Close-packed hexagonal,  $a=8.54$  Å,  $c=15.91$  Å (1)

Hexagonal,  $a=8.66$  Å,  $c=5.32$  Å (2)

Tetragonal,  $a=17.26$  Å,  $c=9.97$  Å (3)

and a structure which may

be an incipient stage of (3) (4).

Typical heat treatments which produced specimens involving the above four crystals are:

heating at 280°C (nominal) for 80 hr (i)

heating at 280°C (nominal) for 168 hr., (ii)

(i) corresponding to the lattices (1) and (2), and (ii) corresponding to (3) and (4), respectively.

The lattice (2) will be an ordered structure of (1), since the former gives many superlattice spots in addition to strong fundamental spots of (1). The lattice (4) is peculiar in that the weak spots, indicative of long range translational symmetry, are not commensurate with the sublattice of strong spots ( $d=2.9$  Å) which surround them, and which agree well with lattice (3). Finally, other investigators have stated that Mn atoms simply diffuse into the Bi crystals and the MnBi crystals form by solid-state reaction.

07.2-9 ADSORPTION MECHANISM OF THIOL COLLECTORS ON METAL AND SULFIDE SURFACES. By S. Anderson\*), K. Laajalehto, L.-S. Johansson and E. Suoninen, Department of Physical Sciences, University of Turku, Finland.

The mechanism of the adsorption of thiol collectors used in flotation of sulfide minerals has been studied by IR methods and more recently by electron spectroscopic methods. Different interpretations have been presented from such measurements for the structure of the adsorption layer resulting from the contact of copper or sulfide surfaces with aqueous potassium ethyl xanthate  $C_2H_5OCS_2K$  solution. According to Mielczarski et al. (*Appl. Surf. Sci.*, 1983, 17, 160-174), the first monolayer consists of xanthate ions adsorbed intact on the surface, whereas Pillai et al. (*Appl. Surf. Sci.*, 1983, 16, 322-344) interpret their results for a PbS substrate as adsorption of diethyl dixanthogen groups, with a subsequent reaction leading to an adsorption layer consisting of diethyl disulfide.

In the present work, the line shape of the S2p XPS emission was measured for an ethyl xanthate layer adsorbed on a copper substrate. The observed line shape can be well fitted with only one  $2p_{3/2,1/2}$  doublet, which indicates that both S atoms of the  $CS_2$  group contribute equally to the adsorption bond. The corresponding measurement for a dixanthogen layer, prepared by evaporation in the instrument vacuum, and a previous measurement for gaseous dixanthogen (Suoninen et al., *J. Electron Spectr.*, 1985, 32, 259-272) both indicate two unequally bonded S atoms with a binding energy difference of about 1.5 eV in both cases.

Hence, the present results support the model of the adsorption layer consisting of ethyl xanthate ions rather than diethyl dixanthogen groups in case of a copper substrate.

\*) Present address: Department of Chemistry  
La Trobe University  
Bundoora, Australia