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ANTIMONY INDUCED CRYSTALLIZATION OF AMORPHOUS SILICON

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Antimony induced crystallization of PVD (physics vapor deposition) amorphous silicon can be observed on sapphire substrates. Very large crystalline regions up to several tens of micrometers can be formed. The Si diffraction patterns of the area of crystallization can be observed with TEM (transmission electron microscopy). Only a few and much smaller crystals of the order of 1 μm were formed when the antimony layer was deposited by MBE (molecular beam epitaxy) compared with a layer formed by thermal evaporation. The use of high vacuum is essential in order to observe any Sb induced crystallization at all. In addition it is necessary to take measures to limit the evaporation of the antimony.

KEY WORDS *antimony; polycrystalline; silicon; thin film*

1. Introduction

Metal induced crystallization (MIC) of amorphous silicon has drawn much attention in the formation of thin, large-grained polycrystalline silicon films on foreign substrates. A possible application of the films prepared by this method is their function as a seeding layer for subsequent deposition of an active layer in the fabrication of solar cells[1]. In particular the use of aluminium has been very successful in the preparation of such seeding layers which can then be used for the processing of solar cells with a p^+-p-n^+ structure[2,3].

In the present study, the authors focus on the crystallization of amorphous silicon by interaction with antimony. The selection of antimony was inspired by the fact that it will act as a donor in the poly-crystalline

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silicon layer and thus will make a straightforward process for solar cells with an n^+-n-p^+ structure possible[4].

Sb shows a eutectic phase diagram with silicon similar to the aluminium-silicon phase diagram, with limited mutual solubilities of Sb and Si and no intermediate phases formed. Solid solubility of Sb in Si is very low; maximum equilibrium solubility of Sb in Si is 0.1at.%; up to 2.6at.% is possible with non-equilibrium processes; the solubility of silicon in Sb is negligible. The melting point of antimony is 630.75℃ and the eutectic temperature is 629.56℃. There have been very few reports on the use of Group V elements to assist with the crystallization of amorphous silicon layers. Gong *et al.*[5,6] and Carlsson *et al.*[7,8] have reported the interaction of Sb with silicon and formation of crystalline silicon films on a Si_3N_4 coated-silicon wafer. Depending on the relative thickness of the Sb and a-Si layer and the heating rate, a crystalline silicon layer or formation of an amorphous Si-Sb phase was observed. Metastable crystalline intermediate phases were not reported.

2. Experimental

Of particular concern is the relatively high vapour pressure of Sb in the temperature range of interest from 400 to 600℃ *e.g.*, the vapour pressure of Sb at 500℃ is 0.3Pa so that in a dynamic vacuum an antimony layer of a few tens of nanometres can easily evaporate completely within a time of the order of tens of minutes. In the present work the amorphous silicon layer was always on top of the antimony layer. This provided an effective seal against evaporation of the antimony on smooth substrates. On substrates with a relatively rough surface, a PVD (physics vapor deposition) silicon layer contained pinholes which could lead to complete evaporation of the underlying Sb layer. The results to be reported here pertain to smooth sapphire 0001 substrates with the *c*-axis at ±0.20°.

Deposition techniques investigated include: (1) MBE (molecular beam epitaxy) Sb by molecular beam epitaxy; thickness was 20 to 50nm with evaporation from a Knudsen cell; substrate was at room temperature; growth rate was around 0.2nm/s. (2) EVA (evaporation) Sb by thermal evaporation in an EDWARDS-SE12E4 vacuum coating unit; thickness was 20 to 70nm; base-pressure was 0.01Pa; substrate at room temperature; (3) PVD a-Si using e-beam evaporation in a Pfeiffer PLS 580 unit; typical thickness was 150nm; base-pressure was 10^{-3}Pa after 1h pumping using a turbo-pump backed by a rotary pump; acceleration voltage of electrons was −10kV; deposition rate was 0.4nm/s; substrate at about 50℃; samples were rotated during deposition for better homogeneity.

Heat treatments were carried out "*in situ*" in a Johanna Otto" 2.4 furnace attached to a Seiffert 3003 TT XRD (X-ray diffraction) diffractometer; base pressure 10^{-3}Pa by turbomolecular pump. The morphology, the structure and composition of the samples were examined using SEM (scanning electron microscopy) and TEM (transmission electron microscopy). Also the influences of various experimental conditions were investigated, such as temperature, time, and the relative thickness of the layers.

3. Results and Discussion

Overlap between prominent Sb and Si peaks rendered the X-ray data gathered during annealing less useful than could have been. Because the Sb peaks are more numerous, one could keep track of the crystallinity of the antimony layer during and after the experiments. Because of the peak overlap, the X-ray data could not provide unequivocal proof of the formation of crystalline silicon. Positive indications of the crystallization of silicon could be provided by SEM observations which were confirmed by TEM study.

The morphology of the surface of the sample after deposition is shown in Fig.1. In Fig.1 nodular very