07.2-5 THE REPRODUCIBILITY OF $CuInSe_2$ THIN FILMS BY RF-SPUTTERING. By T. Warminski*, M. Kwietniak*, R. Beaulieu and J.J. Loferski, Department of Engineering Brown University, Providence, R.I. 02912, USA. * Present address: Telecom Australia Research Laboratories, Clayton, Australia.

$CuInSe_2$ is a promising material for use as an absorber in thin film solar cells (T.J. Coutts, L.L. Kazmerski and S. Wagner, eds., Solar Cells, 1986, 16, 1-640). The method of deposition of the films is important for the realization of high performance cells. The films can be deposited by several techniques: vacuum evaporation, flash evaporation, molecular beam epitaxy, spray pyrolysis and rf-sputtering. Rf-sputtering; We used annealed and cold-pressed targets and water cooled cathode. Argon ions bombarded a target, dislodging atoms and/or molecules with a kinetic energy enough to allow them to reach the substrate (anode), about 5 cm away from the target. Rf-voltage was used to accelerate the argon ions and to generate the plasma. The other parameters were as follows: Ar^+ pressure $5x10^{-2}$ Torr, rf-power $5W/cm^2$, rf-voltage 800V and substrate temperature 293K. A principle of rf-sputtering states that the films should replicate the composition and, therefore, the electrical properties of the target. This will be true provided the target does not decompose during ion bombardment. Otherwise, films produced from the same target under what appear to be identical conditions will in fact be different. The scanning electron microscope (AMR-1000) equipped with EDAX analyser was used to provide images as well as compositions of $CuInSe_2$ targets and the deposited layers. Computer processed EDAX data yield concentrations of Cu, In and Se, within an accuracy of $\pm$ 1% ; A "fine" target (with grain sizes of less than 74 μm) has been analysed after six rf-sputtering cycles. The total duration of sputtering was around 360 minutes. The central part was found filled with needle-shaped grains, each one with a ball-tip (composition, in atomic %: 61-Cu, 8.2-Se, 30.8-In). In the same target and close to the rim there was a black stripe. SEM has revealed that its colour was due to some dust-like material (composition in atomic %: 36.7-Cu, 25-Se, 38.3-In), which apparently had been re-deposited from the vapours. Thus, starting from a moment when the grain tips had melted, the vapours were produced simultaneously by rf-sputtering and evaporation. According to Strelchenko et al. (Izv. Acad. Nauk SSSR, Neorg. Mater., 1969, 5, 593) $CuInSe_2$ dissociates when heated producing Cu (solid), and In_2Se and Se vapours. Rf-deposited layers; J.J. Loferski et al. (Application of Surface Science, 1985, 22/23, 645-655) have demonstrated that sputtering results in deposition of $CuInSe_2$ films of stoichiometric compositions, having grain sizes of the 1-10 μm range. Yet, in the present paper we report on some layers having not always such superior parameters. The morphology of the layers was studied by SEM/EDAX and the structure by X-ray diffraction. It was observed that in the case of the "fine" target the reproducibility of $CuInSe_2$ thin films primarily depends on chemical uniformity of the target.

07.2-6 CRYSTALLOGRAPHY OF TiNx FILMS IN EXCESS OF NITROGEN. By R. R. Manory and G. Kimmel, Nuclear Research Centre-Negev, Beer-Sheva, Israel, 84190.

The crystal structure of TiN is known to be of the NaCl type, in correlation with the ratio between the atomic radii of its components. It is described as a close - packed isometric structure of titanium, in which nitrogen occupies all octahedral sites. This phase is stable for x values between 0.6 to 1.2 , where over - stoichiometry is explained by vacancies in the titanium lattice.

In the present work the existence of a new structure of the CaF_2 type was revealed in the Ti - N system. This structure was observed in thin films obtained by reactive sputtering, using high levels of nitrogen in the plasma. It was found to be stable at room temperature, transforming into the normal NaCl structure when heated. The characteristics for amorphous and crystalline films are presented in detail.

07.2-7 GRAZING INCIDENCE X-RAY DIFFRACTION STUDY OF INTERFACIAL SUPER STRUCTURE: a-Si ON $Ge_{0.2}Si_{0.8}$ (111)-5x5. By K.Akimoto, J.Mizuki, T.Hirosawa, T.Tatsumi, N.Aizaki and J.Matsui, Fundamental Research Laboratories, NEC Corporation, Japan.

It has been shown (K.Akimoto, et al., to be published in Surf. Sci.) that the 5x5 interfacial super structure exists on the amorphous Si(a-Si)/$Ge_{0.2}Si_{0.8}$(111) interface. In this report, we will show the further experimental results. Two dimensional 1/5th-order Bragg peaks were measured by the grazing incidence X-ray diffraction technique. The experiment was carried out using synchrotron radiation from the PF (Photon Factory) storage ring in Japan. The specimen, a-Si/$Ge_{0.2}Si_{0.8}$/Si(111) was prepared by MBE technique. Before a-Si film of 100 Å in thickness was deposited, the 5x5 reconstructed surface structure of $Ge_{0.2}Si_{0.8}$/Si(111) was confirmed by a RHEED pattern. A total of 68 interface Bragg intensities were measured. It was found that the intense peaks lay around fundamental lattice points ((10),(01),(11) etc.) and on the line connecting fundamental lattice points in the two-dimensional reciprocal lattice space. The present result agrees with that of the TED observation (K.Kajiyama, et al., The Annual Meetings of the Physical Society of Japan, March, 1986.) of 5x5 surface structure. However, the (4/5,4/5) Bragg peak was intense while the (3/5,3/5) was not observed, which is not consistent with the TED observation mentioned above. This difference may imply that the deposition of a-Si results in destroying the periodic order of adatoms which are believed to exist in a DAS model (K.Takayanagi, et al., J.Vacuum Sci. Technol. A3 (1985) 1502.). We are now proceeding the detailed analyses.