NEW AMORPHOUS SILICON BASED ALLOY

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Abstract

Amorphous hydrogenated silicon (a-Si:H) prepared by glow discharge decomposition of SiH_4 has been modified by adding the SbF_5 to the SiH_4. By this way it is possible to change the conductivity by many orders of magnitude. So Sb acts as a dopant but moreover at sufficiently high SbF_5 to SiH_4 ratios the a-Si:H is modified - the Sb-Si alloy with strongly decreased optical gap is produced.

Introduction

Amorphous hydrogenated silicon (a-Si:H) is a perspective material for terrestrial photovoltaic solar cells. There are two regions of physico-chemical problems which has to be studied to get efficient a-Si:H based photovoltaic cells. First of all - the question of effective doping and the second, not less important - possibility of modification,mainly decrease of band gap of a-Si:H, because of optical absorption edge of a-Si:H is rather high ($E_g \approx 1.7$ eV).

A series of modified a-Si:H based materials have been produced by glow discharge decomposition of SiH_4 with SiH_2Cl_2, SiH_3CH_3, CH_4, CO, SiF_4, N_2, BF_3 and GeH_4 for example /1/ but nobody has tried until now the SbF_5 mixture with SiH_4. Cosputtering of Sb has been used to dope a-Si:H prepared by sputtering /2/ and implantation of Sb into a-Si:H has been made /3/ too.

Experimental

The samples have been prepared by glow discharge in a slightly modified diode system, comparable to that one described by Fritzsche /4/. The quartz substrates have been placed on upper (floating) electrode (diameter of 8,5 cm) and approximately 1 cm below this one the powered electrode (cathode) of 8 cm diameter has been placed. All the presented results have been measured on samples prepared at substrate temperature $T_s = 320^oC$, which together with the frequency 2MHz, power about 0.5 W/cm^2 and 2 sccm flow rate of pure SiH_4 (Matheson) corresponds to the optimized preparation conditions of photosensitive undoped a-Si:H.

SbF_5 is a liquid at room temperature with the vapour pressure approx. 420 Pascal ($\approx$3.1 Torr). The flow rate of SbF_5 vapours was controled by the needle valve. The ratio of the flow rates of SbF_5 and SiH_4 we suppose to be equal to the volume ratio of SbF_5/SiH_4. The pressure in a reactor was 10 and 40 Pascal before and after the plasma starting respectively.

Typical sample thickness was 2 μm (measured with TALYSURF) the growth rate was about 1.3 μm per hour. All samples had a mirror-like surface except the sample with the highest SbF_5 concentration. So the optical measurement on this sample which have shown only weak interference fringes is only qualitative (curve #5, Fig. 2).

The measurements of the d.c. electrical conductivity has been done on a "gap" type samples prepared on a quartz substrates, using gold as a contact material.

Optical transmission spectra from 0.5 to 2.3 μm have been measured on a double beam spectrophotometer and then analysed according to /5/, averaging of interference fringes has been done. The optical absorption edge E_g has been determined from the intercept of $\alpha^{1/2}.E^{1/2}$ with the E axis, where $\alpha(E)$ is absorption coefficient at photon energy E.

Absorption coefficient α in a low absorption region has been measured by constant photocurrent method (CPM), experimental details of which will be published elswhere /6/. This method is suitable for our photosensitive samples. The spectra were matched to transmission measurements in $\alpha \doteq 10^3$ cm^{-1} region.

Results and discussion

From Fig. 1 it is seen that with increasing SbF_5/SiH_4 ratio room temperature d.c. electrical conductivity rapidly increases and approaches to $10^{-3} \div 10^{-2} \Omega^{-1} cm^{-1}$ range. Correspondingly activation energy E_{RT} defined by the relation $\sigma_{RT} = \sigma_0 \cdot \exp(-E_{RT}/kT)$ decreases from 0.8 eV for undoped a-Si:H to $0.2 \div 0.3$ eV. This can be explained by the movement of Fermi level from the centre of gap close to the conduction band as follows from the simple check of the thermopower sign. The sample with highest Sb content slightly below room temperature changes activation energy to $E \doteq 0.11$ eV, which we suppose correspond to the energetical distance of donor Sb level from the conduction band, labeled as E_{Sb} in Fig. 1. Rather surprising is fact, that at low Sb content the conductivity decreases before the strong increase is started. Prefactor σ_0 is for undoped a-Si:H $\sigma_0 \approx 2.10^4 \Omega^{-1} cm^{-1}$, but for Sb doped a-Si:H σ_0 is from $100 \div 300 \Omega^{-1} cm^{-1}$. This can be explained by the transition to the trap limited mobility, because the number of traps is probably increased by the increasing number of donor levels below the conduction band edge.

Spectral dependence of the optical absorption coefficient $\alpha(E)$ in the 10^{-1} to 10^5 cm^{-1} range is shown in Fig. 2. Density of the gap states N(E) and band states $N_{CB}(E)$, $N_{VB}(E)$ is directly related to $\alpha(E)$. We suppose that in low absorption region we measure by CPM the electron transitions from filled states under Fermi level to conduction band states with $N_{CB} \approx 10^{21}$ cm^{-3} eV^{-1} /7,8/. Shoulder in N(E), $0.4 \div 0.7$ eV above valence band, commonly found in a-Si:H glow discharge or sputtered samples and seen in photoconductivity and absorption measurements in the 1.1 - 1.4 eV region /7,8/ is found also in our samples.

It follows from Fig. 2, curves #1 and #2, that our undoped or very slightly doped samples have a low density of gap states N(E), which is about 10^{17} cm^{-3} eV^{-1} in above region. With rising SbF_5 to SiH_4 ratio this shoulder grows up (curve #3), in addition with creation of donor level close to the conduction band as follows from conductivity measurements. Similar behaviour has been found in phosphorus doped a-Si:H and simple model was presented /8/. But with further increase of SbF_5 to SiH_4 ratio (curves # 4 and # 5) the optical gap shifts to the lower energy, from 1.85 eV to 1.68 eV (# 4) and to ≈ 1 eV (#5). So the SbF_5 acts as an optical gap modifier.

Conclusions

It has been demonstrated, by the measurements of electrical conductivity, optical transmission and CPM that by the addition of SbF_5 to SiH_4 samples of a-Si:H produced by the glow discharge decomposition of this mixture are Sb doped. At high SbF_5 to SiH_4 ratios the Sb modified a-Si:H is produced, with significantly lower absorption edge ($Eg \approx 1$ eV). Until now only the addition of GeH_4 to SiH_4 decreased the absorption edge so significantly. Further investigations are in course and will be published later.

References

/1/ D.P. Tanner, G.R. Johnson and M.P. Sefcik, Solar Energy Materials 3, No 4. (1980), 533

/2/ Nguyen Van Dong, Tran Quoc Hai, J. of Non-Cryst. Sol. 35 & 36 (1980), 351

/3/ P.G. Le Comber, W.E. Spear, G. Müller and S. Kalbitzer, J. of Non-Cryst. Sol. 35 & 36 (1980), 327

/4/ C.C. Tsai and H. Fritzsche, Solar Energy Materials 1 (1979), 29

/5/ R. Tsu, W.E. Howard and L. Esaki, Phys. Rev. 172, (1968), 779

/6/ M. Vaněček, J. Kočka, J. Stuchlík and A. Tříska, submitted to Sol. St. Communications

/7/ P.O´Connor and J. Tauc, Solid State Commun. 36 (1980),947

/8/ D.A. Anderson, G. Moddel and W. Paul, J. of Non-Cryst. Sol. 35 & 36 (1980), 345.

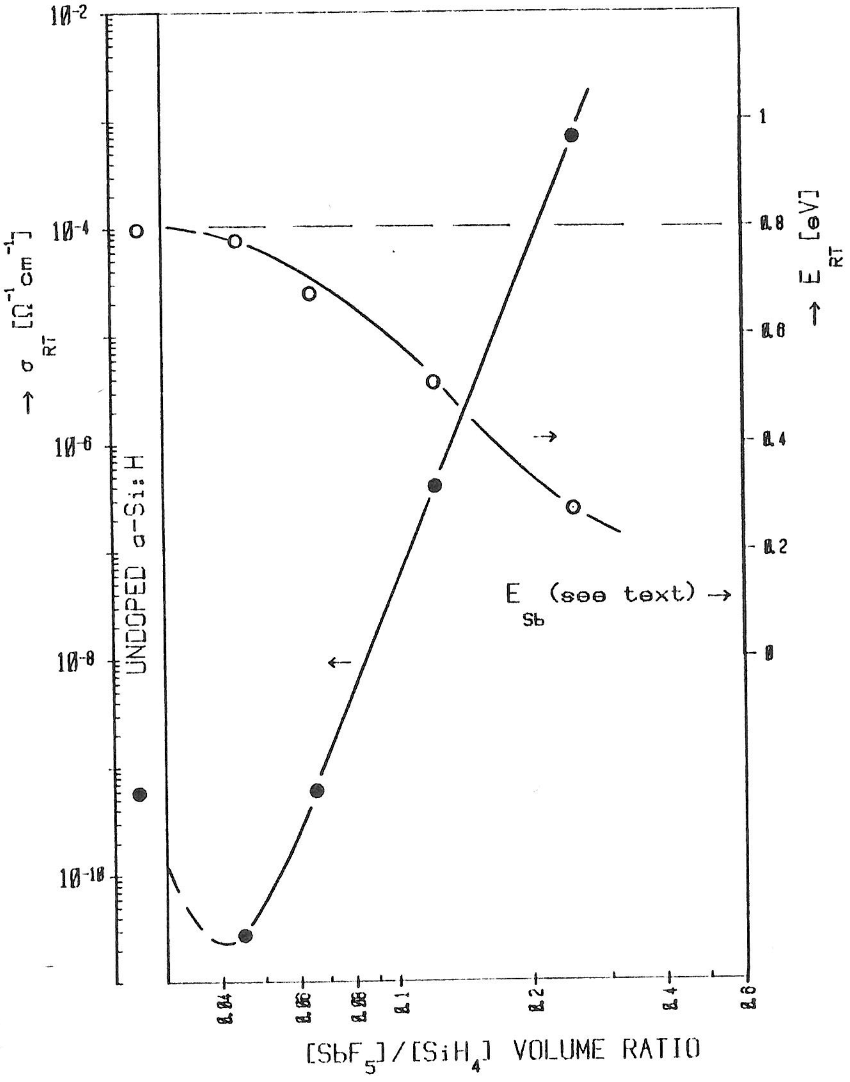

Fig. 1
Room temperature d.c. electrical conductivity σ_{RT} and its activation energy E_{RT} of Sb doped (modified) a-Si:H as a function of SbF_5/SiH_4 volume ratio.

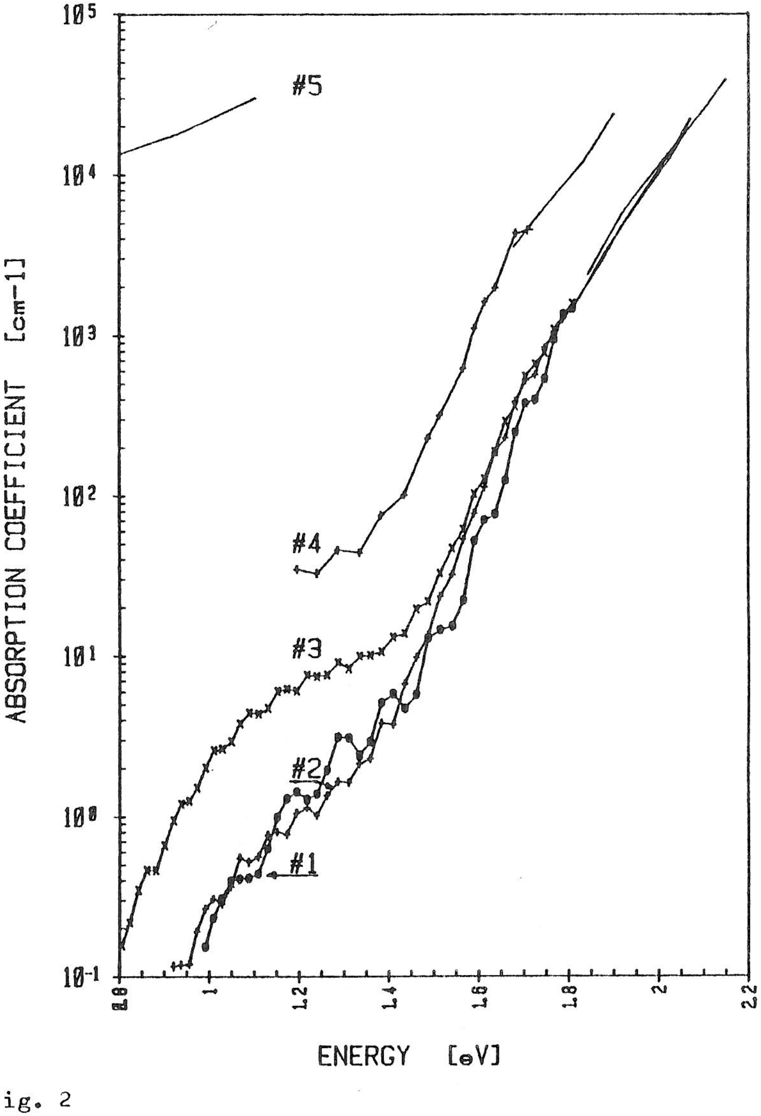

Fig. 2
Spectral dependence of optical absorption coefficient $\alpha(E)$ determined from transmission measurements (full curves without points) and from CPM (bellow $\alpha \doteq 10^3$ cm^{-1}). Curve # 1 (000) is undoped a-Si:H, doping by SbF_5 increases from curve # 2 (+++) to # 5. Corresponding SbF_5 to SiH_4 volume ratio is seen in Fig. 1.