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"Hydrogenated Amorphous Germanium and Its Alloys"

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HYDROGENATED AMORPHOUS GERMANIUM AND ITS ALLOYS

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ABSTRACT

This paper refers to the opto-electronic properties of hydrogenated amorphous germanium and its alloys (deposited by the rf-sputtering method). It is shown that enormous progress has been made in the optimization of a-Ge:H films, even though they are not yet a fully electronic quality material. The problems of material stability and doping are discussed in the light of recent results. The important issues of hydrogenated Ge-Sn and Ge-N alloys are presented, as well as recent results in the a-Ge:H device area.

INTRODUCTION

Today, hydrogenated amorphous silicon (a-Si:H) is an electronic semiconductor of controllable quality. On the basis of the present knowledge of the physics and chemistry of a-Si:H films, remarkable progress has been made in manufacturing devices, such as high efficiency *p-i-n* solar cells, thin film transistors, and imaging devices. Nowadays, the industrial applications of amorphous semiconductors film represent a market of around one billion dollars. The commercial perspectives of solar electricity generation are still brighter. The unavoidable depletion of fossil fuel reserves and the constraints imposed on nuclear fuels by the environment make the photovoltaic conversion of sunlight one of the most interesting energy alternatives.

The need of efficient, cheap, and stable materials for the photovoltaic conversion of sunlight led many research groups to investigate new compound amorphous semiconductors. Variable band-gap amorphous alloys of electronic quality are essential in the manufacturing of efficient multiple junction (or tandem) solar cells. The electric output of tandem solar cells can be notably increased by a proper choice of the opto-electronic properties of the layers composing the structure. Even for single gap solar cells, the properties of the active layer has to be matched to the spectral distribution of sunlight in order to get an optimized electric power output.

Most of the research efforts on semiconductor alloys have been directedtowards the understanding, and eventual mastering, of the properties

of silicon-germanium alloys (a-Si:Ge:H). Amorphous Si-Ge alloys possess optical properties intermediate between those corresponding to both elemental semiconductors. Until now, however, success has been rather limited. It has been found that the band gap can be easily tailored in the (1.1 - 1.8)-eV energy range . The electronic properties of the alloys, on the other hand, deteriorate enormously on alloying. In addition, deposition conditions leading to high quality a-Si:H films produce very defective a-Ge:H material. It is conceivable that deposition of Ge atoms with good local surroundings require quite different plasma conditions, and also quite different plasma-surface interactions, than that for the deposition of Si. As a consequence, a few research groups decided to investigate and optimize the end component a-Ge:H, so as to discover the appropriate conditions for device quality film deposition. Our team in Campinas has made great progress in preparing such films by rf sputtering [1]. It has also been demonstrated that a-Ge:H films of improved quality may be prepared by the glow discharge decomposition of GeH_4 [2] in reactors having a special geometry. The present paper intends to summarize the main properties of rf-sputtered a-Ge:H films and to review recent results of our research team in the deposition of a-Ge:H alloys and devices.

DEPOSITION CONDITIONS AND CHARACTERIZATION

A-Ge:H samples are deposited by rf sputtering a pure crystalline Ge target of 99.9995% nominal composition, in an argon (minimum purity: 99.997% + hydrogen (99.9995%) atmosphere. A Leybold-Heraus model Z-400 apparatus is used. Before each deposition run the system is pumped down to a total pressure $P_T < 10^{-6}$ mbar for several hours and the residual gases analyzed with a Edwards EQ 80F mass spectrometer. The most important residual-gas partial pressures correspond to argon ($P_{Ar} \cong 5 \times 10^{-7}$ mbar), and by nitrogen ($P_{N2} \cong 10^{-7}$ mbar). All other contaminants, up to an atomic mass 80 display partial pressures below 10^{-7} mbar. The growth rate is adjusted before each deposition run and measured again after the end of the process. A growth rate of 1 Å/s and a substrate temperature of around 200 C were adopted for the studies on a-Ge:H and Ge alloys. Samples are typically 1 μm thick. RF-sputtered chromium coplanar ohmic contacts are normally used to measure the electronic properties of the films.

The dark conductivity [(120-400)-K range] is measured in an evacuated chamber, using a Keithley model 617 electrometer connected to a microcomputer. Besides the acquisition of electrical data and the corresponding sample temperature, the computer is used to control the rate of temperature variation

of the samples (typically 3 K/min). Before these measurements the samples are annealed during 20 min at 400 K.

Polished intrinsic c-Si wafers are used as substrates for IR optical transmission measurements in the (400-4000) cm^{-1} wave-number range. These measurements are performed either in dispersive or in interferometric Fourier-transform spectrophotometers. Optical measurements in the nir-vis region of the spectrum are made on films deposited onto Corning 7059 glass substrates. The concentration of hydrogen atoms bonded to Ge is determined from the integrated absorption of the Ge-H wagging vibration mode in the mid infrared region [3]. The total hydrogen content of some selected samples is determined from Elastic Recoil Detection analysis and thermal effusion techniques.

OPTO-ELECTRONIC PROPERTIES OF INTRINSIC a-Ge:H FILMS

Figure 1 shows an Arrhenius plot of the dark conductivity of an a-Ge:H sample of improved quality. An activated type conductivity is measured down to low temperatures, an indication of the low density of defects at the Fermi energy. The activation energy stays around 0.5 eV, i.e. slightly above the optical Tauc (1.1 eV) mid-gap . The low density of deep defects in these samples is corroborated by sub-gap optical absorption. Figure 2 shows the absorption coefficient as determined from photo thermal deflection spectroscopy (PDS) and the constant photo current method (CPM). The integrated absorption in the sub-gap region, converted in the usual way into a density-of states (DOS) in the gap, indicates $3x10^{16}$ cm^{-3}. This value is to be compared with values of $5x10^{15}$ cm^{-3} for state-of-the-art a-Si:H. The one order of magnitude increase in gap DOS is much smaller than the measured decrease in steady-state photo conductivity σ_{pc} (about a factor of 10^2), an indication that other factors contribute to the deterioration of the electronic transport. Parenthetically, it has to be remembered that a high photo-to-dark conductivity ratio is a necessary but not a sufficient condition for a good photovoltaic material. The majority carrier mobility-lifetime product may be artificially increased by defect centers that kill the transport properties of the opposite carrier. As the collection of both carriers is essential in solar cells a more complete description is needed, which necessarily include the position of the Fermi energy and the density of gap states.

The Urbach edge parameter, which roughly represents the disorder broadening of the bands is, for optimized a-Ge:H films of the order of 50 to 55 meV, which is not much higher than for high quality a-Si:H (45-50 meV). The relatively poor σ_{pc} of a-Ge:H is a consequence of a carrier mobility μ_n of

a-Ge:H being much smaller of that of a-Si:H (less than 10%). The reasons for the difference are not yet fully understood. Table I summarizes the optical and transport properties of state-of-the-art rf-sputtered a-Ge:H films.

HYDROGENATION AND METASTABILITY

Hydrogen plays a fundamental role in the optoelectronic and structural properties of tetrahedrally bonded amorphous semiconductors. H atoms remove part of the weak bonds and passivate dangling orbitals, relaxing the structure and improving the electronic properties (see figure 1). Much of the information available about Ge-H bonds comes from IR absorption measurements[4]. a-Ge:H samples display three absorption bands: two of them corresponding to Ge-H stretching vibration modes centered at 1880 cm^{-1} and at 1970 cm^{-1}, respectively, and the third associated to the Ge-H wagging mode centered at 565 cm^{-1}. The high frequency stretching mode is associated with Ge-H bonds at the surface of large voids, while the 1880 cm^{-1} mode corresponds to hydrogen bonded in voids of the size of a vacancy. The intensity ratio of both absorption peaks is related to the film density and with structural homogeneity. A-Ge:H films with good photo-electronic properties possess a large $\alpha_{1880}/\alpha_{1970}$ ratio. No bending modes [(750-850) cm^{-1} range] associated with $Ge-H_2$ groups are found in such films.

As is well known, electronic defects can be created in a-Si:H by exposing the material to either intense illumination, or electric fields, or currents, or rapid thermal quenching [5]. In all cases the defects can be removed by annealing at temperatures above 150 °C, a temperature that characterizes the metastability. Metastability is at present a major barrier to the large scale application of a-Si:H solar cells, and considerable effort is being made to understand its microscopic origin.

A natural question that arises is whether a-Ge:H films of improved quality also exhibit the same kind of metastable behavior in electronic properties as a-Si:H. Our research group in Campinas extended the investigations on metastable effects to the case of a-Ge:H [6]. The kinetics of light-induced defect creation and of their thermal relaxation was established. It was found that a-Ge:H films of electronic quality degrade in a way similar to a-Si:H when light-soaked. Both the dark conductivity and the photo conductivity decrease after exposure to light. The original values are recovered after thermal annealing of the samples at 120 °C , although the effect has no thermal origin. The light-induced degradation resembles the Staebler-Wronski effect[5] in a-Si:H, where the reduced conductivity is due to

the creation of defects in the pseudo-gap (dangling bonds). The kinetics of defect generation and relaxation in a-Ge:H are well represented by a stretched-exponential time evolution. The characteristic time constants for the conductivity variation during light soaking and annealing are temperature activated. The activation energies, however, differ from those currently measured in a-Si:H.

An extensive study on the diffusion of hydrogen and deuterium in the a-Ge:H network was recently done by Graeff *et al.*[7]. The driving idea was to determine whether the metastable effects in the films were mediated by the diffusion of hydrogen through the network, as proposed by the *hydrogen glass* model[8] . In other words, if the light degradation of the electronic properties of a-Ge:H were mediated by the diffusion of hydrogen,- what would be the diffusion coefficient and its temperature dependence allowing to account for the experimental metastability data ?. The diffusion coefficient of hydrogen in the amorphous germanium network was found to be dispersive: $D_H(t) = D_0(\omega t)^{-\alpha}$, as expected, with a dispersion parameter α = 0.95 at 280 °C. D_H at a constant diffusion length (L = 60 nm) is temperature activated, with an activation energy of 0.44 ± 0.09 eV. This value is in good agreement with the characteristic decay time constant of the conductivity variations during light soaking and annealing[6] $E_A(\tau)$ = 0.44 eV. However, no definite conclusions can be drawn at present because the thermal annealing experiments are made at temperatures above deposition temperature and irreversible structural changes occur during the process. The experiments of light-induced defect creation, on the contrary, are performed at much lower temperatures where no structural changes are measured. More studies are in progress to clarify the problem.

DOPING

Solid state electronics relies on the possibility of altering the electric properties of intrinsic semiconductors via doping with chemical impurities. The usual doping process, however, is different in an amorphous semiconductor than in a crystal in the sense that the crystal constraints of symmetry force an impurity atom of different valence to have the same coordination number as its host in a substitutional covalent site. In amorphous networks the local minimization of free energy may also be attained with the impurity atom having a first coordination number equal to its chemical valence (self-compensated site)[9-11]. Both types of sites coexist in amorphous networks and their relative stability results from the combined short-range chemical contributions and the lattice strain. According to

Street[11] the position of the Fermi energy plays a fundamental role in determining the relative density of each type of site, from which the active doping efficiency is a function of the impurity concentration.

The doping mechanisms and the doping efficiency of Group III and Group V elements of the Periodic Table in a-Si:H films have been extensively studied. Much less work has been done on the other elemental amorphous semiconductor a-Ge:H. The role of phosphorus and boron as active dopants in the a-Ge:H network has been studied by Jones *et al.*[12], and by Stutzmann *et al.*[13], among others. It is worth mentioning that those studies were performed on highly defective a-Ge:H films having a DOS in the pseudo-gap of around 10^{18} cm^{-3}. It is our opinion that doping experiments in amorphous semiconductors require: *i*) a starting intrinsic material having a low DOS (this requirement has almost never been met in the case of a-Ge:H); *ii*) a relatively low DOS in the doped samples (as a consequence, the dark conductivity must be thermally activated, at least, at room temperature and above); *iii*) an overall impurity content corresponding to true doping levels (typically below 0.5 at.%), rather than higher concentrations leading to the alloy phase; and *iv*) the same degree of hydrogenation in all samples (many of the changes measured in the transport properties of doped samples may be the consequence of a different degree of hydrogenation and not of impurity activity). Not all these requirements have been sufficiently considered in studies concerning doping effects in amorphous semiconductors.

The doping properties of nitrogen[14] and aluminum[15] in a-Ge:H have been recently studied in our research group. Figure 3 shows an Arrhenius plot of nitrogen-doped a-Ge:H films. It may be seen that the introduction of minute amounts of N in the a-Ge network produces large conductivity changes. The room temperature conductivity experiences a two order of magnitude increase and the activation energy at RT and above decreases from E_a = 0.5 eV (intrinsic film) to E_a = 0.11 eV for the most effectively N-doped film. The conductivity of intrinsic and lightly N-doped a-Ge:H samples show a single activation energy in the (120-400)-K range. At temperatures below 250 K heavier N doping induces a second conduction path through localized states near the conduction band edge. The analysis of the transport data indicates that, in an active dopant configuration, nitrogen produces a shallow donor level located at around 50 meV below the conduction band edge. The Fermi energy of N-doped a-Ge:H shifts almost 400 meV with doping, an indication of a very efficient process. The doping efficiency is the ratio of active/total nitrogen concentration. Figure 4 shows the nitrogen doping efficiency in a-Ge:H as a function of the impurity

concentration in the solid phase[16]. The total nitrogen content of the samples was determined from a deuteron induced nuclear reaction [$^{14}N(d,p)^{15}N$]. The doping efficiency of phosphorus in the a-Si:H network is also shown for comparison.

Summarizing, a-Ge:H films of improved quality can be as effectively doped as a-Si:H films. This finding opens new opportunities for device applications.

ALLOYING

The properties of germanium-nitrogen, germanium-tin and, to a lesser extent, germanium-silicon alloys have been also investigated in Campinas. It is not possible to give here a full account of all the research results. Let us simply mention the most relevant aspects related to the perspectives of Ge alloys as electronic materials.

$a\text{-}Si_{0.1}:Ge_{0.9}:H$ films were prepared under conditions giving good a-Ge:H. This Ge rich alloy posses a pseudo-gap of around 1.2 eV, and interesting value for the bottom cell of a tandem structure. Preliminary results[17] indicate, however, that there is a deterioration of the overall opto-electronic properties. Work is in progress to optimize the alloy deposition conditions.

Amorphous alloys having an energy gap smaller than 1.1 eV would be useful in the fabrication of cheap infrared sensors. Narrow band-gap amorphous semiconductors are obtained by alloying Si or Ge with tin. The study of the composition, the structure, and the electrical and optical properties of a-Ge:Sn:H [18-21] indicate that there is little hope of an electronic quality narrow energy-gap amorphous semiconductor alloy. The addition of small amounts of Sn atoms (doping levels) to the a-Ge:H network kills the photoconductivity of the films and induces conduction paths through states in the gap[18]. Mössbauer studies of a-Ge:Sn alloys indicate that most Sn atoms go substitutionally in the a-Ge network. However, a second resonance corresponding to a chemical environment similar to the one found in β-Sn indicates a defective configuration, which occurs because of trapping of Ge vacancies by Sn atoms. The final configuration is a Sn atom in the center of a relaxed Ge divacancy bonded to six neighboring Ge atoms. The existence of such unavoidable defect is responsible for the degradation of the transport properties because of new electronic states in the pseudo-gap. The conclusions of the a-Ge:Sn:H study are far reaching in the sense that they establish new limits to the technology of variable band-gap amorphous alloys. These limits are imposed by the most stable chemical configuration of foreign atoms at the normal and at the *defective* sites of elemental semiconductor networks. Let us

remark that these defective sites are unavoidable in over constrained tetrahedrally coordinated amorphous alloys.

The pseudo-gap of a-Ge:H may be widened by alloying with nitrogen [22], the germanium nitride having a forbidden energy larger than 4 eV. Our research group has been studying the structural and opto-electronic properties of a-Ge:N:H along recent years. Highly diluted N in the Ge network produces the doping effects already described. The alloy phase is dominated by trigonally coordinated nitrogen, the valence band being most probably dominated by *N 2p* non-bonding states. As expected, non-stoichiometric alloys exhibit a very large structural disorder due to the presence of atoms of quite different size and valence structure. We do not foresee electronic applications for amorphous Ge-N alloys, with the possible exception of passivating layers.

DEVICES

The final test for an electronic material is the possibility of fabricating good devices. To our knowledge only one group made *p-i-n* diodes having an a-Ge:H film as an active layer[23]. The reported conversion efficiency of such devices is 3.2 % .We have recently made surface barrier devices with Pd and Ag as metal electrode[24] . The electrical characteristics of a Ag/a-Ge:H Schottky diode is shown in figure 5. Rectification ratios as high as 250 at 0.8 V have been achieved, an indication of the excellent quality of the barrier. The structure shown in figure 5 degrades with time. We believe this to be due to metallic migration into the a-Ge:H network. More work is under way to improve the device performance and to fabricate *p-i-n* devices.

CONCLUSIONS

Although the research efforts on a-Ge:H have been much less intensive than those made on a-Si:H, important progress have been recently made in the understanding of the opto-electronic properties of a-Ge:H alloys. The state-of-the-art material has properties not yet as good as a-Si:H but, in our opinion, there is room for further improvements. In this sense, a fully electronic quality a-Ge:H alloy is still to come. Several research groups are working in this direction. If they are successful a precious material will be available for the manufacturing of efficient and cheap solar energy conversion devices.

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TABLE I: Optoelectronic properties of rf-sputtered a-Ge:H films

H_2(IR)	σ_d	E_a	$N(E_F)$	E_U	σ_{pc}/σ_d	E_g(Tauc)	E_{04}
(at.%)	$(\Omega.cm)^{-1}$	eV	cm^{-3}	meV	(ELH)	eV	eV
7-10	10^{-5}	0.5	$4x10^{16}$	53	1.3	1.1	1.2

FIGURE CAPTIONS

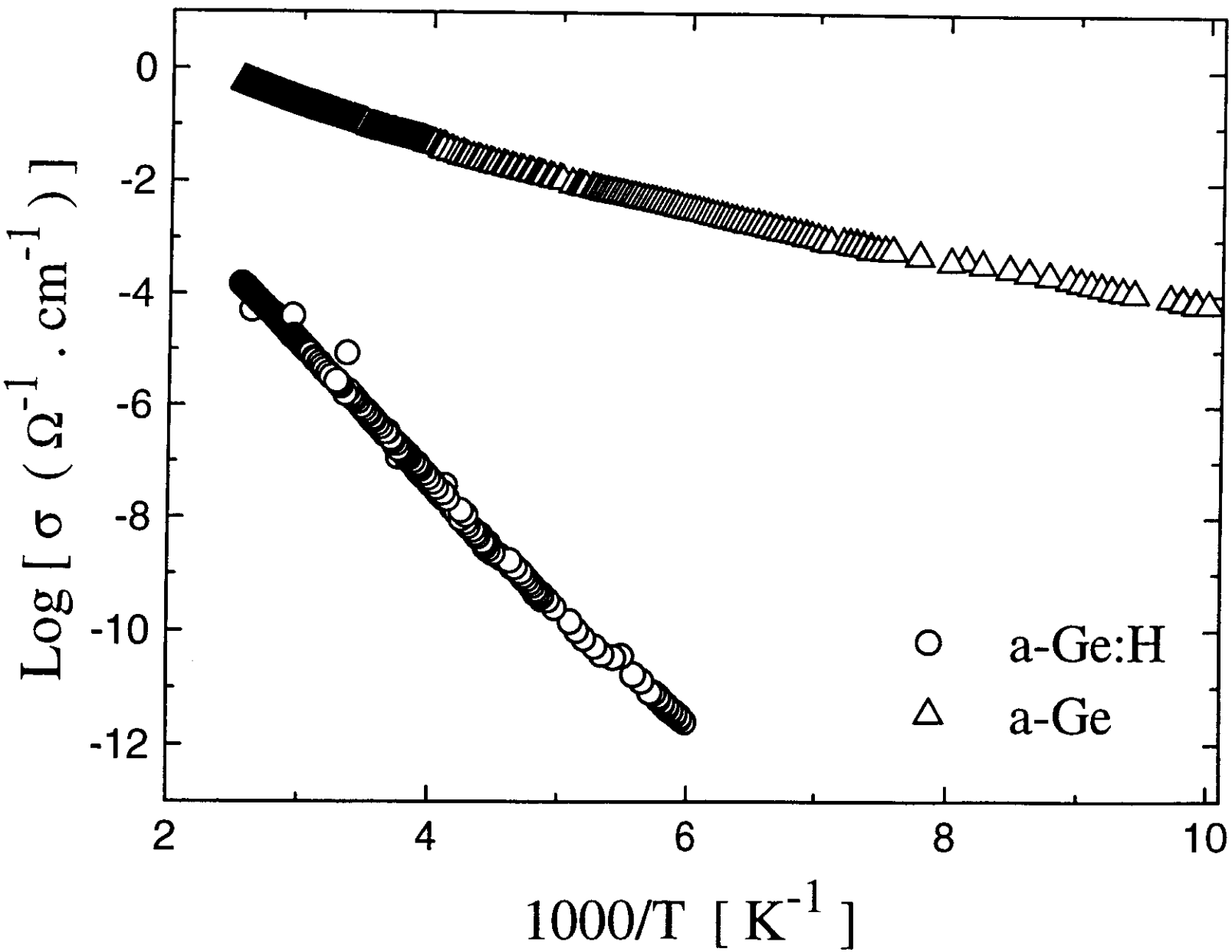
Figure 1.- Logarithm of the dark conductivity versus inverse temperature for an a-Ge:H film. Note the thermally activated conduction down to low temperatures. The conductivity of an un-hydrogenated a-Ge film is shown for comparison.

Figure 2.- Logarithm of the absorption coefficient versus the photon energy of a good quality a-Ge:H film. The absorption edge has an exponential like dependence on energy, with a characteristic energy E_o = 53 meV. The sub-gap absorption has been determined from photothermal deflection spectroscopy (PDS) and constant photocurremt method (PCM) data.

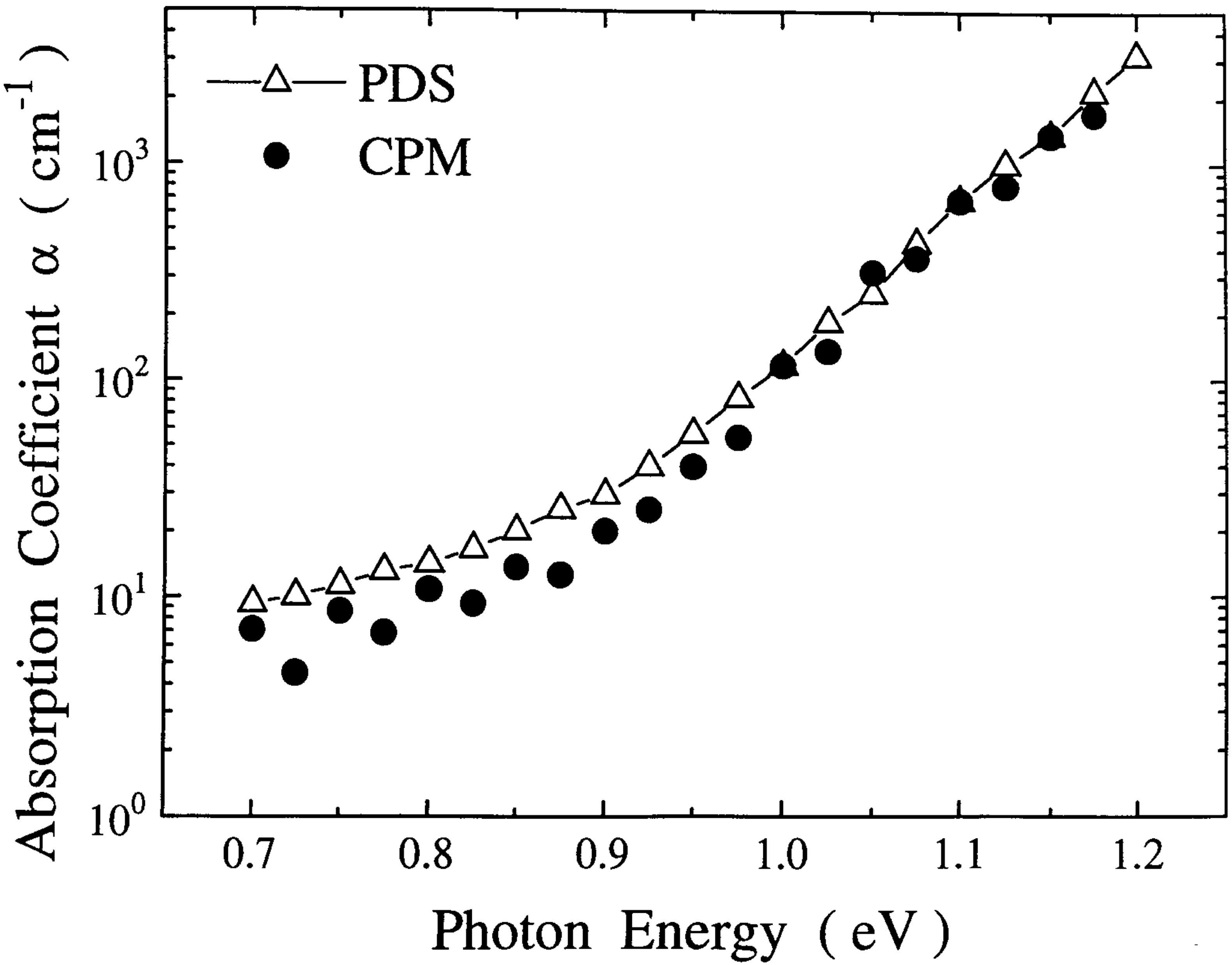
Figure 3.- Logarithm of the conductivity versus inverse temperature for an intrinsic a-Ge:H sample (# 1) and for N-doped films. Note the overall increase in conductivity and the decrease of the activation energy of the lightly doped material (# 2), which corresponds to an upward shift of the Fermi energy. A heavier n-doping (# 4) induces a conduction path through localized states at low temperatures.

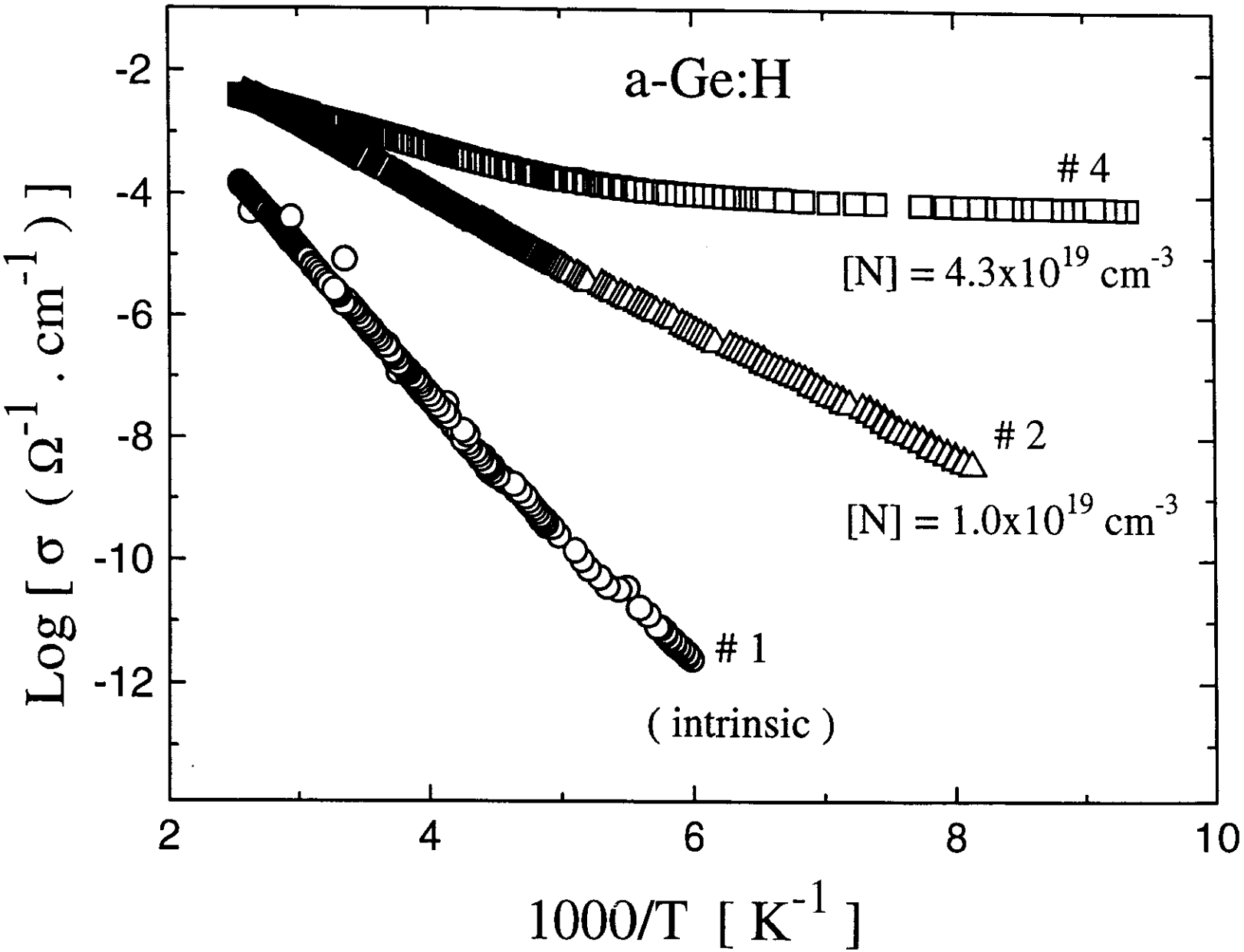
Figure 4.- Doping efficiency vs nitrogen concentration in the solid phase for N-doped a-Ge:H films (squares). The doping efficiency of phosphorus doped a-Si:H is shown for comparison (triangles).

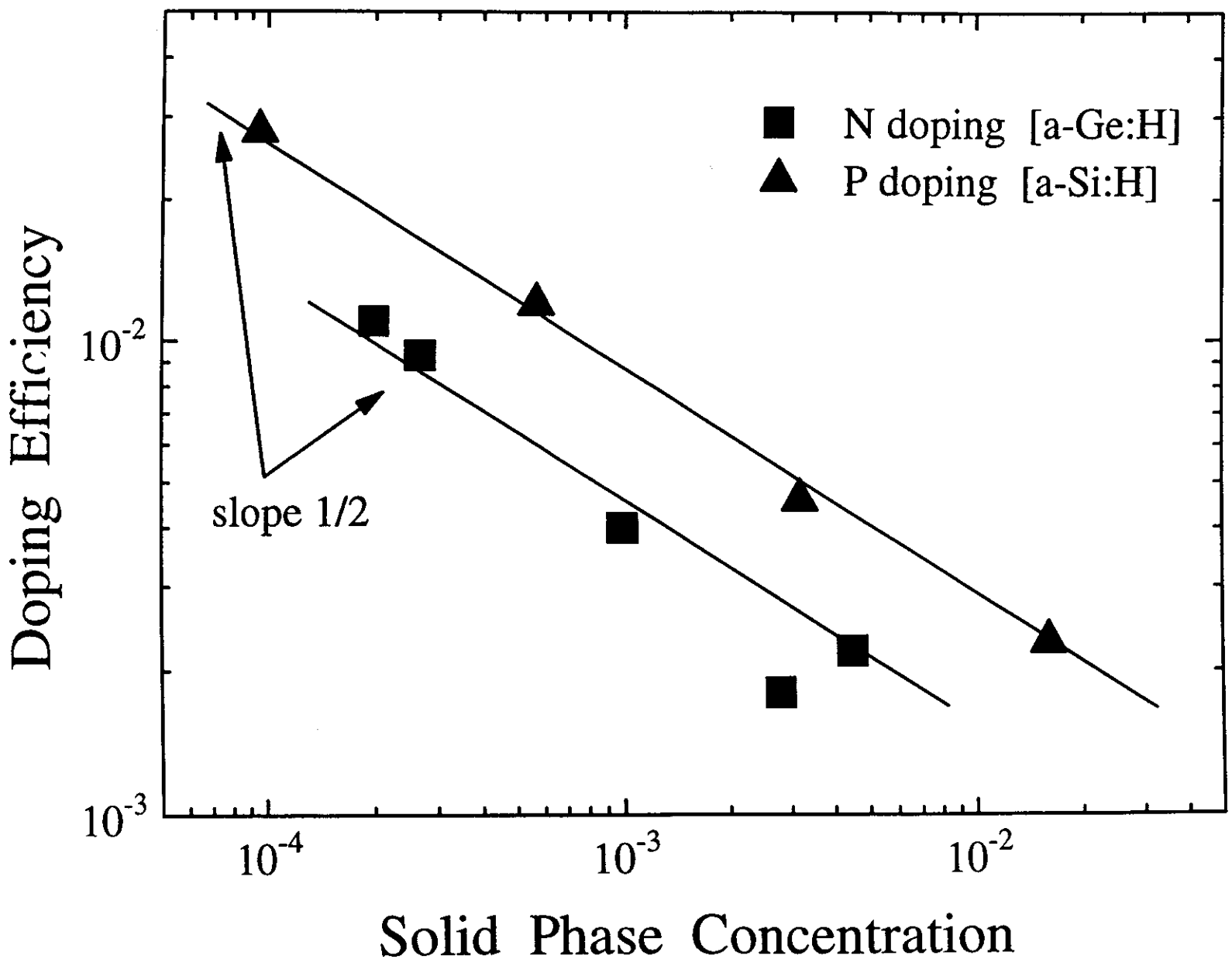
Figure 5.- Electrical characteristics of a Ag/a-Ge:H Schottky barrier diode with the structure shown in the inset.



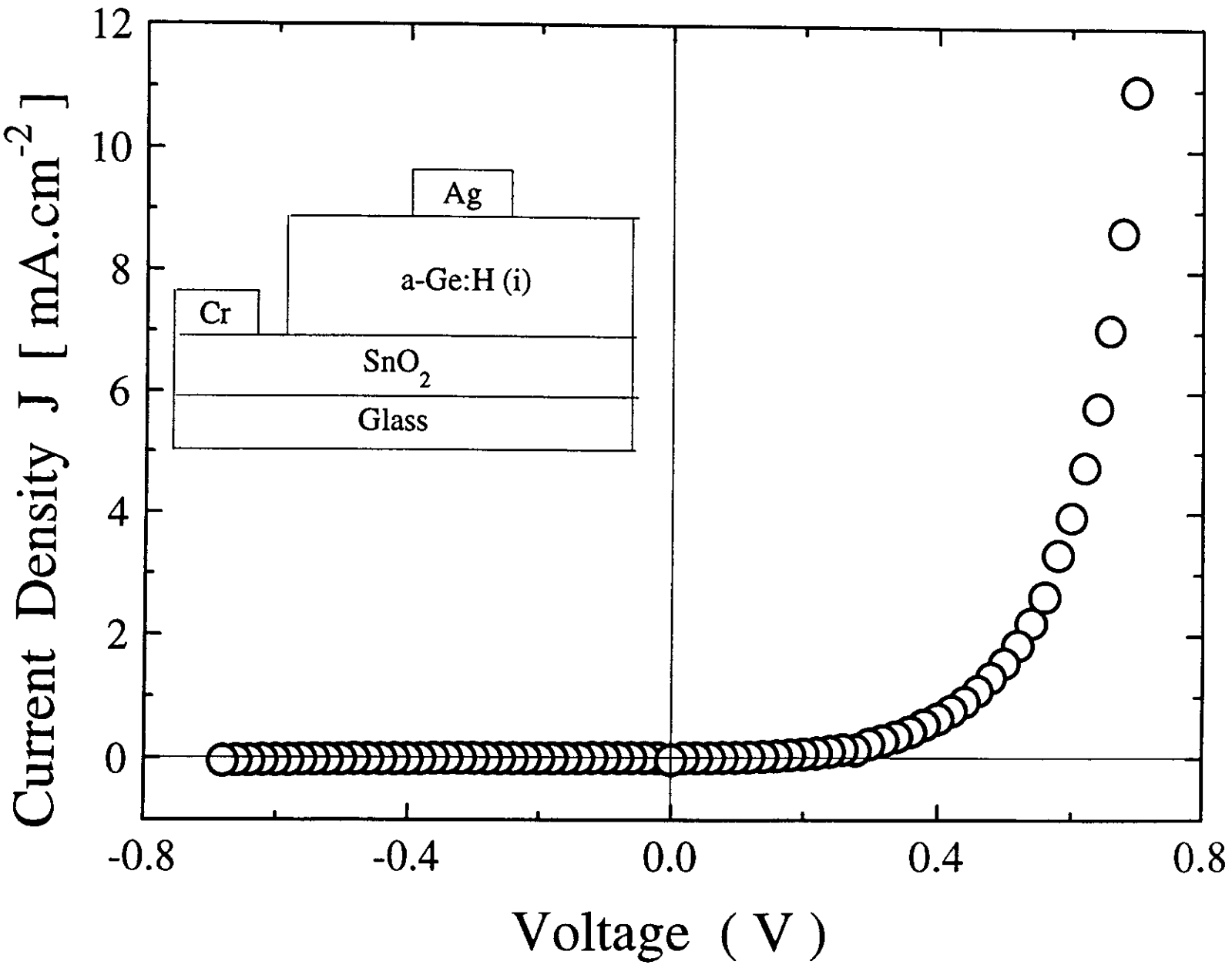
Chamboulleyron Fig 14


PDS
CPM
Absorption Coefficient α (cm-1)
10^3
10^2
10^1
10^0
0.7
0.8
0.9
1.0
1.1
1.2
Photon Energy (eV)


a-Ge:H
# 4
[N] = 4.3x10^19 cm^-3
# 2
[N] = 1.0x10^19 cm^-3
# 1
(intrinsic)
Log [σ (Ω^-1 . cm^-1)]
-2
-4
-6
-8
-10
-12
2
4
6
8
10
1000/T [K^-1]



Chamboulevron. Fig 4



Chamboulevron Fig 5