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Nature of the Impurity States Arising from Transition Metals in Hydrogenated Amorphous Silicon

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Introduction The doping of hydrogenated amorphous silicon (a-Si:H) has been subject of numerous investigations for the last decade /1/. The basic technique for the effective control of the electrical properties of a-Si:H is doping from gas mixtures /2/. In this and other doping techniques, most of the impurity atoms in the a-Si:H network are in electrically inactive states and deteriorate the electrical and optical properties of the materials. For this reason, impurity atoms in both inactive and active states should be investigated. In this connection, experimental techniques identifying charge and coordination states of impurity atoms in amorphous solids are very attractive.

This note gives results on the doping of a-Si:H with transition metals (iron, europium, ytterbium) by means of the sputtering technique. Two charge states, Me^{2+} and Me^{3+}, are typical of these metals which could result in their similar behaviour as impurities. On the other hand, the different electron structure of these elements, i.e. unfilled 3d shell for Fe and 4f shell for Eu and Yb, could lead to some features in their action on the electrical properties of a-Si:H.

Along with conventional measurements of electrical and optical properties of doped a-Si:H, we used the Mössbauer spectroscopy for the ^{57}Fe and ^{151}Eu impurity atoms. Preliminary results were published in /3/.

Experimentals Films of a-Si:H:Me (Me = Fe, Eu, or Yb) were prepared by rf co-sputtering of metallic and monocrystalline silicon targets in a gas mixture of Ar, H_2, and SiH_4. The substrate temperature T_s was 250, 300, or 380 °C. The concentrations of the metal impurity and hydrogen were 0.1 and 10 at%, respectively. The microstructure of the films was observed by a GSM-5 electron microscope. All investigated films were homogeneous with an accuracy of 40 to 60 nm. The homogeneity of the films was not affected by the doping.

Both the dark conductivity σ_d and photoconductivity σ_{ph} were measured in a planar geometry. The photoconductivity was measured at 295 K under irradiation by light with λ = 0.65 μm and an intensity of 4×10^{17} photons/cm^2. The dc dark conductivity was determined in the temperature interval of 100 to 500 K. The optical absorption edge was determined at 295 K.

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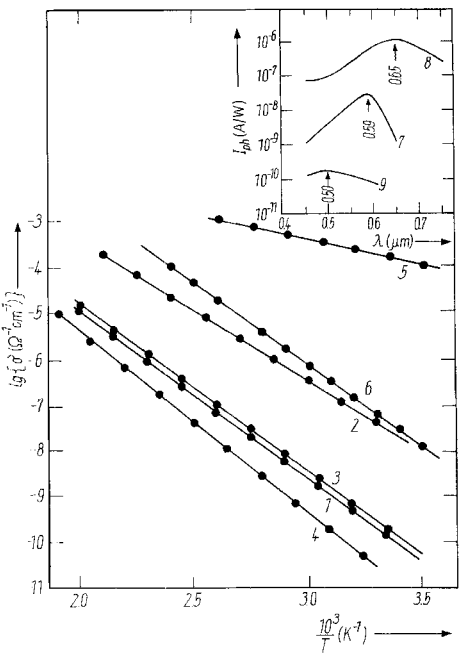


Fig. 1. Temperature dependences of the dark conductivity of the a-Si:H films: (1), (2) undoped, (3), (4) iron doped, (5) europium doped, (6) ytterbium doped; substrate temperatures T_s: (1), (3) 250 °C, (2), (4) to (6) 380 °C. The insert shows the room temperature spectral photoconductivity of the undoped (7), iron doped (8), and europium doped (9) films prepared at T_s = 380 °C

The Mössbauer spectra of the ^{57}Fe and ^{151}Eu impurity atoms were measured at 80 and 295 K with ^{57}Co and $^{151}Sm_2O_3$ sources, respectively. The isomer shifts are given relative to α-Fe and Eu_2O_3.

Experimental results and discussion

According to the thermoelectric power measurements, the undoped a-Si:H samples had n-type conductivity. The Seebeck coefficient was negative at 295 K with an absolute value of about 200 μV/K. As it is seen from Fig. 1, the temperature dependences of the dark conductivity at 100 to 500 K are described by $\sigma_d = \sigma_o \exp(-E_\sigma/kT)$, where E_σ is the activation energy. These facts could be conventionally explained by an electron conductivity of the undoped films through extended states lying higher than the mobility edge E_c with the activation energy $E_\sigma = E_c - F$, where F is the Fermi level. The parameters σ_o and E_σ as well as σ_{ph} are appreciably dependent on T_s (see Table 1). The optical gap for the films is (1.72 ± 0.02)eV independently of T_s.

The doping of a-Si:H by iron does not change the sign of the Seebeck coefficient and the optical gap value. The temperature dependence of the dark conductivity of the iron doped films is described by an Arrhenius law similar to the undoped films. However, the effect of T_s on σ_o, E_σ as well as on σ_{ph} is opposite to the effect for the undoped films (see Table 1). For the iron doped films, the activation energy E_σ increases and the photoconductivity σ_{ph} decreases with increasing T_s. The effect of iron is most remarkable at T_s = 380 °C. The structure of the Mössbauer spectra of ^{57}Fe impurity atoms in the a-Si:H films is affected by T_s. For the films prepared at T_s = 250 and 300 °C, they are quadrupole doublets with the isomer shifts σ = (0.20 ± 0.02) mm/s and the quadrupole splitting Δ = (0.34 ± 0.03) mm/s. The parameters of the spectra are typical for Fe^{3+} in a non-cubic surrounding and practically independent of the substrate temperature and the measuring temperature. Similar spectra for crystalline silicon doped with ^{57}Co /4/

T a b l e 1

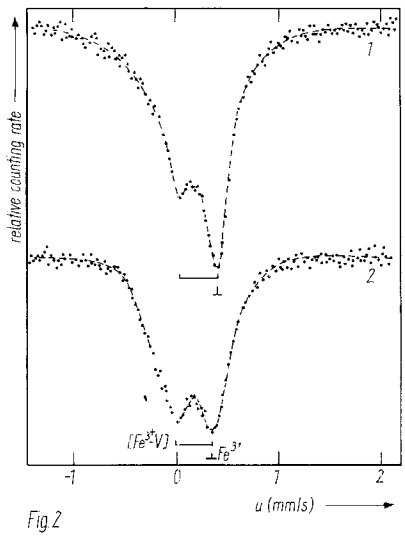
Conductivity characteristics of a-Si:H films

composition	T_s(°C)	E_σ(eV)	σ_o ($\Omega^{-1}cm^{-1}$)	$\sigma_{295\ K}$ ($\Omega^{-1}cm^{-1}$)	σ_{ph}/σ_d
a-Si:H	250	0.70	$1.8x10^2$	$1.5x10^{-10}$	10^4
a-Si:H:Fe	250	0.69	$2.0x10^2$	$1.9x10^{-10}$	$5x10^2$
a-Si:H:Eu	250	0.68	$1.3x10^3$	$1.0x10^{-9}$	$5x10^2$
a-Si:H	300	0.71	$1.3x10^3$	$6.3x10^{-10}$	10^4
a-Si:H:Fe	300	0.69	$8.9x10^1$	$9.5x10^{-11}$	$5x10^2$
a-Si:H:Eu	300	0.56	$3.2x10^2$	$5.0x10^{-7}$	$8x10^3$
a-Si:H	380	0.58	$2.8x10^2$	$3.4x10^{-8}$	10^4
a-Si:H:Fe	380	0.80	$3.2x10^2$	$1.9x10^{-11}$	$5x10^2$
a-Si:H:Eu	380	0.20	$5.6x10^{-1}$	$5.0x10^{-4}$	10^3
a-Si:H:Yb	380	0.70	$4.3x10^4$	$2.0x10^{-9}$	10^2

were ascribed to an electrically inactive iron-vacancy associate. We suggest the same interpretation for the above quadrupole spectra in a-Si:H. The electrical inactivity of iron in this state is supported by a weak effect of the impurity on the conductivity of the films prepared at T_s = 250 and 300 °C (see Table 1).

The spectra of the iron doped films prepared at T_s = 380 °C have an additional singlet with σ = 0.35 mm/s (see Fig. 2) typical for Fe^{3+}. The singlet line corresponds to isolated iron atoms with a high symmetry of their surroundings.

The relative concentration of the isolated iron atoms is negligible at $T_s \leqq 300$ °C because the vacancy-like defect concentration is high enough to capture all iron atoms. At T_s = 380 °C, the defect concentration drops and a noticeable part of the iron atoms remains in the isolated state. According to the relative intensity of the singlet line this part is about 5%. Since the iron doping affects remarkably the conductivity only for films having a singlet component in the Mössbauer spectra the isolated iron atoms should be accepted electrically active. Their electrical activity could be ascribed by an acceptor level or band within the mobility gap of a-Si:H. The Fe^{3+} singlet should correspond to a neutral state of the iron acceptor centers. A Fe^{2+} line that should have resulted from the ionized state of the acceptor centers lacks in the Mössbauer spectra. This fact indicates a low population of the acceptor band, i.e. the Fermi level lies at the bottom of the band. It means that the iron acceptor concentration is much greater than the concentration of intrinsic states lying between the Fermi level positions in the undoped and doped films. The position of the iron acceptor band relative to E_c could be taken from the activation energy E_σ = 0.80 eV for the films prepared at T_s = 380 °C (see Table 1). This



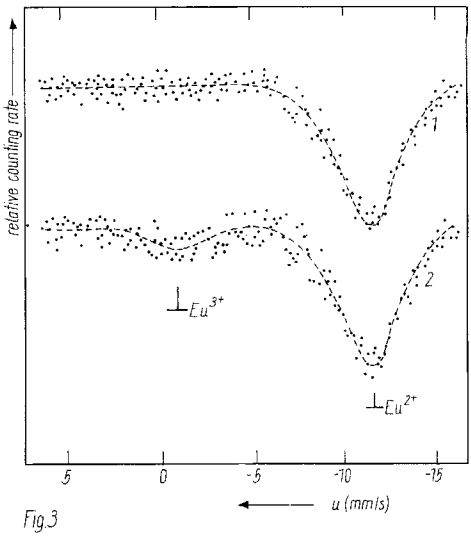


Fig. 2. Room temperature Mössbauer spectra of ^{57}Fe impurity atoms in a-Si:H films prepared at T_s = 250 °C (1) and 380 °C (2)

Fig. 3. Liquid nitrogen temperature Mössbauer spectra of ^{151}Eu impurity atoms in a-Si:H films prepared at T_s = 250 °C (1) and 380 °C (2)

value is an upper estimation for $E_c - E_{Fe}$ (where E_{Fe} is the iron band energy) because the major part of the iron acceptors is in the neutral state and, thus, the Fermi level could lie lower than E_{Fe}.

Another effect of the iron impurity is the decreasing photoconductivity in the a-Si:H films (see Table 1). The iron impurity seems to form recombination centers which could arise from both above iron states because the photoconductivity drops for the doped films prepared at all substrate temperatures under investigation.

In contrast to iron, the europium impurity atoms increase the conductivity of a-Si:H. The doping effect rises with increasing T_s similar to the iron case (see Fig. 1 and Table 1). The Seebeck coefficient and the optical gap are independent of the doping. It means that the europium impurity in a-Si:H shifts the Fermi level to E_c. This effect could be explained by a donor level or band in the upper part of the mobility gap. Electrons of the band fill underlying intrinsic defect states of a-Si:H and lift the Fermi level. The doping efficiency in such a model should increase with decreasing concentration of the intrinsic defects what is observed in our experiments as the dependence of F on the substrate temperature for the europium doped films (see Table 1). Europium builds up a relatively shallow donor band in a-Si:H. Its position $E_c = E_{Eu}$ could be estimated from the activation energy E_σ = 0.2 eV

for the films prepared at T_s = 380 °C. For this reason an activity of europium as a recombination center is low and only the σ_{ph}/σ_d ratio decreases, but the absolute value of the photoconductivity increases at europium doping. The insert at Fig. 1 shows the spectral dependences of the photoconductivity for undoped and europium doped a-Si:H films. It is essential that a red shift of the spectra is observed for the doped films apart from the enhanced photoconductivity.

The Mössbauer spectra of the ^{151}Eu impurity atoms in a-Si:H show two lines corresponding to Eu^{2+} with δ = -11.7 mm/s and to Eu^{3+} with δ = -1.7 mm/s (Fig. 3). The spectra of the films prepared at T_s = 250 °C consist of the only Eu^{2+} line. Since the doping efficiency at T_s = 250 °C is very low, the Eu^{2+} state should be ascribed to electrically inactive europium centers. The width of the Eu^{2+} line, Γ = 3.6 mm/s, is almost three times greater than the natural width, Γ_{nat} = 1.3 mm/s. The broadening indicates the association of the europium atoms with structural defects, for example, with vacancy-like ones or oxygen pollution. The electrically inactive Eu^{2+} centers bind the defects and clean the mobility gap improving the photoelectrical properties of a-Si:H as discussed above. The Mössbauer spectra of the films prepared at T_s = 300 and 380 °C have the Eu^{2+} as well as the Eu^{3+} lines. The relative intensity of the Eu^{3+} line increases with increasing conductivity of the films. Thus, this line should be ascribed to electrically active Eu centers and, taking into account the donor activity of Eu, to an ionized state of the europium donor centers. A neutral state of the donor centers, i.e. a second Eu^{2+} line in the Mössbauer spectra, is not observed because the Fermi level does not reach the europium donor band.

Thus, both iron and europium build up in a-Si:H electrically active centers with the neutral states corresponding to ions with half-filled electron shells (Fe^{3+}, $3d^5$ for iron and Eu^{2+}, $4f^7$ for europium). In this connection, ytterbium is a very interesting impurity in a-Si:H. It has two normal valence states - Yb^2 with the closed $4f^{14}$ electron configuration and Yb^{3+} with the $4f^{13}$ configuration. The ytterbium centers might be predicted to have a neutral state with the closed $4f^{14}$ electron configuration and, therefore, a donor activity at a transition to an ionized state with the $4f^{13}$ configuration. In contrast to this prediction, ytterbium shows an acceptor activity in a-Si:H shifting the Fermi level down to E_c - 0.70 eV (see Fig. 1 and Table 1). In addition, it decreases the photoconductivity similar to the iron impurity.

One should note again that the major part of the iron and europium impurity atoms in a-Si:H are electrically inactive. This electrically inactive majority is formed by association with defects of the amorphous matrix. We can put at the end of the paper the question, whether this mechanism is a common cause of the low doping efficiency of a-Si:H and hydrogenated amorphous materials, in general.

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