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Transport Phenomena in Amorphous Silicon Doped by Ion Implantation of 3d Metals

By

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Charge transport in amorphous silicon (a-Si) doped with ion implantation of Mn^+, Ni^+, Fe^+, and Cu^+ ions is studied using ESR technique, temperature dependence of conductivity $\sigma(T)$, and thermopower $\alpha(T)$ measurements. With increasing of impurity (Mn, Ni, Fe) concentration (from 10^{18} to 10^{19} cm^{-3}) the localized state density and σ decrease owing to the passivation of silicon dangling bonds with impurity atoms. An analysis of conductivity and thermopower data allows to reveal three temperature regions. 1) At $250 < T < 500$ K σ is due to holes excited from the acceptor impurity states. 2) At $T > 500$ K electron transport dominates. 3) At $T < 250$ K hopping conductivity with variable range hopping near Fermi level prevails. For a-Si:Mn in the region of $4 < T < 80$ K Coulomb correlations are detected in the behaviour of $\sigma(T)$. The Coulomb gap is found to reach a maximum value 25 meV which appears to be one order of value larger than the known (one) in semiconductors doped with shallow impurity levels.

С помощью метода ЭПР, измерения температурных зависимостей проводимости $\sigma(T)$ и термо-э.д.с. $\alpha(T)$ исследован перенос заряда в аморфном Si (a-Si), легированном имплантацией ионов Mn^+, Ni^+, Fe^+ и Cu^+. С увеличением концентрации примеси (Mn, Ni и Fe) от 10^{18} до 10^{19} cm^{-3} происходит уменьшение плотности локализованных состояний и σ за счет пассивации оборванных связей при встраивании примесных атомов вблизи дефекта. Анализ $\sigma(T)$ и $\alpha(T)$ показал, что 1) в области $250 < T < 500$ K проводимость определяется дырками, возбужденными с примесных акцепторных состояний; 2) при $T > 500$ K доминирует электронный транспорт; 3) при $T < 250$ K преобладает прыжковая проводимость вблизи уровня Ферми. В области $4 < T < 80$ K в температурной зависимости проводимости a-Si:Mn обнаружено проявление кулоновских корреляций. Установлено, что максимальная величина кулоновской щели составляет $\approx$25 meV, что более чем на порядок превышает значения, известные для систем полупроводник-примесь с мелкими уровнями.

1. Introduction

Transition metals with nonfilled 3d-shell easily interact with lattice imperfections in Si. Recently [1] to [3] it was shown that doping by ion implantation with medium dose or by co-sputtering of 3d-transition metals makes it possible to reduce considerably the localized state density due to dangling bonds. Increasing implantation dose raises the conductivity of amorphous silicon (a-Si) [3]. The dangling bond compensation and high doping efficiency achieved by Mn implantation were discussed in terms of a structural model based on impurity–defect complexes. The behaviour of other first transition row elements is also of interest in a-Si.

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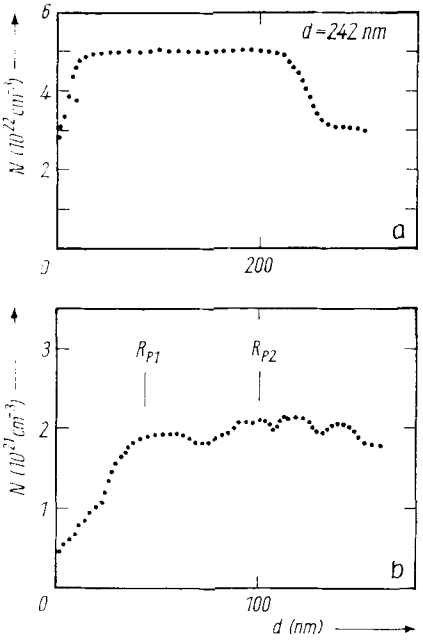

Fig. 1. Spectra of He^+ ions backscattered from a) initial a-Si and b) a-Si:Fe films, R_{p1} and R_{p2} mean projected ranges of Fe^+ ions with energies of 50 and 120 keV, respectively

In this paper the results of study of transport properties of a-Si doped with Mn, Fe, and Ni concentrations from 10^{18} to 6×10^{21} cm^{-3} are reported. The temperature and concentration dependences of conductivity and thermopower were studied in detail.

2. Experimental

The a-Si films were prepared by electron-beam evaporation onto quartz substrates at a pressure of 10^{-4} Pa. The deposition rate and substrate temperature were 0.3 to 0.5 nm/s and 350 °C, respectively. The final thickness of a-Si layers was about 0.25 μm. The amorphous structure of the films was controlled by the electron diffraction technique.

Ion implantation was carried out on the High Voltage Engineering Europa 350 kV heavy ion accelerator. Samples were mounted on a water-cooled target holder. The ion current density at the target was kept below 2.5 μA/cm^2. In order to reach a homogeneous implant concentration in depth multiple energy implantation was used with ion energies ranging from 50 to 230 keV (Fig. 1). The EPR signal was measured in X-band by spectrometer Varian E4502.

3. Results and Discussion

High dangling bond density is typical for undoped a-Si layers (spin concentrations within the range 5×10^{19} to 2×10^{20} cm^{-3}), independently of the preparation technique (deposition in vacuum, ion bombardment of crystalline Si, etc.). In the case when an impurity is chemically active in Si, dangling bond compensation occurs via impurity-defect interaction [2]. It becomes possible when the impurity concentration N is comparable with or larger than the defect concentration N_d. Our EPR measurements show (Fig. 2) the effect of spin compensation which was observed for all elements, excluding argon, in the dose range 10^{15} to 10^{16} cm^{-2} that means implant concentrations $N \geq 10^{20}$ cm^{-3}.

Transition metals Cr, Mn, and Fe are most effective in this respect apparently due to the presence of the nonfilled 3d-shell which is able to form covalent bonds with the unpaired electrons of defects under s–p hybridization [4]. We believe that the effect of compensation is caused by direct binding of an impurity atom with a defect rather than by electron transfer from transition metal atom to defect.

We now consider the electrophysical properties of a-Si doped with metallic implants. Fig. 3 shows that conductivity slightly increasing with implant concentrations from 10^{18} to 10^{19} cm^{-3}. Within the range 1×10^{19} to 2×10^{19} cm^{-3} conductivity has a minimum indicating dangling bond passivation by impurity atoms and suppression of the hopping conduction via localized states. With further increase in transition

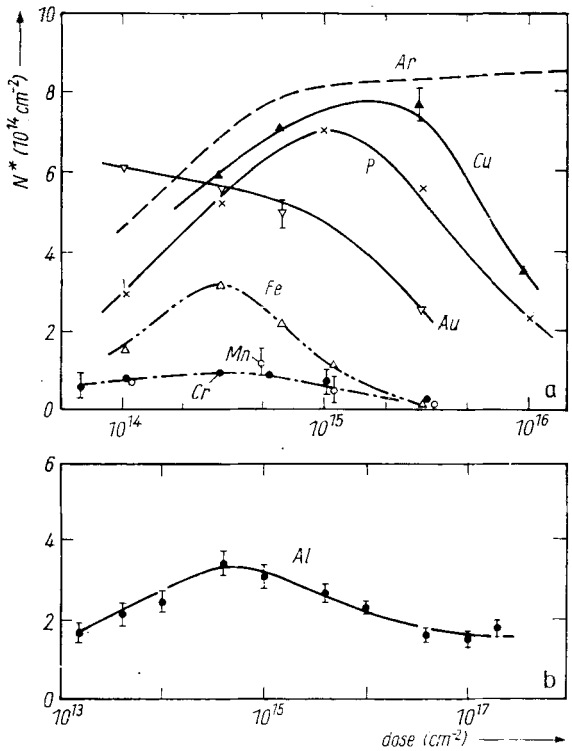

Fig. 2. Dose dependence of number spins in a-Si implanted by different ions of metals (N^* is the sheet spin density. Al was implanted by Dr. A. Mertens (Humboldt University, Berlin). Current densities of Al^+ of 40 $\mu A/cm^2$ were reached at high-dose implantation)

metal concentration the conductivity rises steeply, reaching a maximum value of 60 Ω^{-1} cm^{-1} in a-Si:Mn at $N = 6 \times 10^{21}$ cm^{-3}.

To be sure that the high conductivity was not the result of percolation through metallic phase inclusions, we performed conductivity measurements on a-Si implanted with Al^+ ions, whose concentration reached 10^{22} cm^{-3} (about 20 at%). Aluminium tends to produce metallic phase inclusions at this concentration [5]. The conductivity of a-Si:Al was proved to be three or four orders of magnitude less than that of a-Si:Mn. So the high conductivity in a-Si:Mn could not be connected with metallic phase inclusions.

With Cu^+ implantation the conductivity varies slightly and does not exceed $(2 \text{ to } 3) \times 10^{-4} \Omega^{-1}$cm^{-1}. This result seems to be explained by precipitation of a solid state solution of a-Si:Cu at implantation. A small doping effect is also observed in a-Si:Mg.

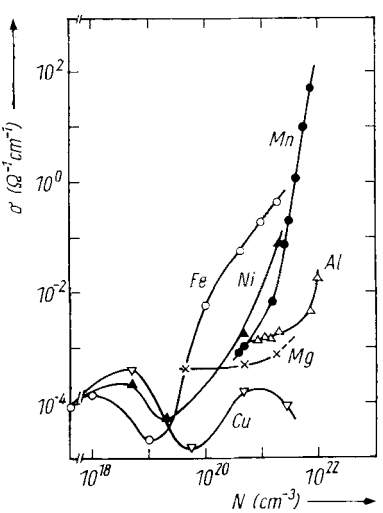

Fig. 3. Conductivity versus implant concentration in a-Si implanted with ions of metals

Another possibility of explanation of the steep increase in conductivity is the silicide formation. Transition metals are known [6] to produce silicide, that are semiconductors with band gap about 0.3 to 0.4 eV excepting nickel silicide whose properties are close to metals. So, if silicides were really produced in our experiments, the conductivity should be a few orders of magnitude higher in a-Si:Ni than in a-Si:Mn and a-Si:Fe at equal concentration of implanted impurities. We obtained practically the same values of σ for these three metals. This points to a low effect of silicide formation. According to [7] silicides were not detected in ion-implanted Si when the concentration of Fe was less than 50 at%. In our study [8] silicide formation was observed in a-Si:Mn with $N = 4 \times 10^{21}$ cm^{-3} after annealing at 350 °C only. Conductivity was decreased at annealing. After higher-temperature annealing the pure metallic phase

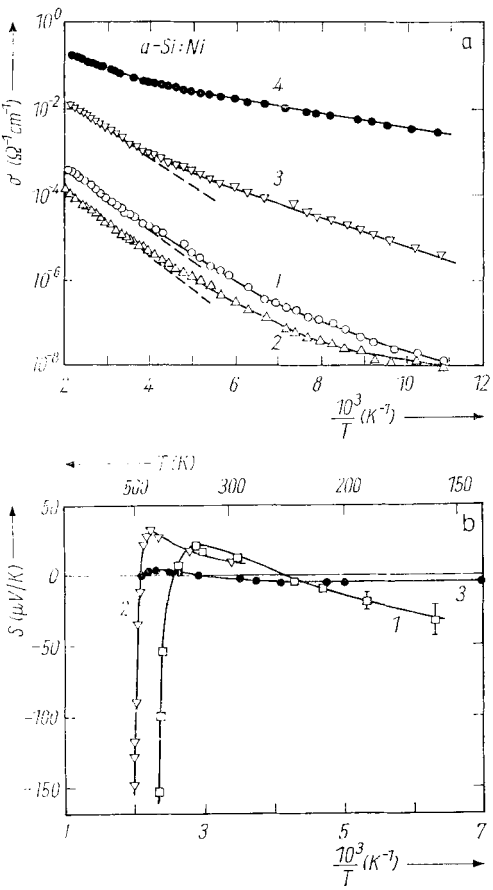

Fig. 4

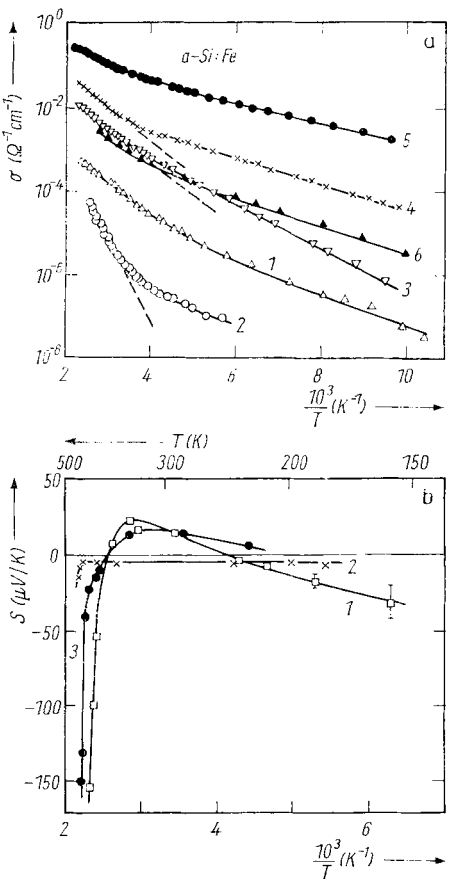

Fig. 5

Fig. 4. a) Conductivity and b) thermopower versus reciprocal temperature in a-Si:Ni. For a) (1) $N = 5 \times 10^{18}$, (2) 2×10^{19}, (3) 5×10^{20}, (4) 2×10^{21} cm^{-3}; for b) (1) initial, (2) $N = 5 \times 10^{20}$, (3) 2×10^{21} cm^{-3}

Fig. 5. a) Conductivity and b) thermopower versus reciprocal temperature in a-Si:Fe and a-Si:Ar. For a) (1) $N = 10^{18}$, (2) 10^{19}, (3) 10^{20}, (4) 5×10^{20}, (5) 2×10^{21} and (6) 10^{21} cm^{-3}; for b) (1) initial, (2) 5×10^{20}, and (3) 2×10^{21} cm^{-3}

Mn was found. Therefore metallic or silicide inclusions should not provide the high conductivity in our samples.

Fig. 4 and 5 show the temperature dependences of conductivity and thermopower of a-Si films implanted with Ni and Fe, respectively. Similar results were obtained in [3] for a-Si:Mn. In the temperature interval $250 < T < 500$ K the thermopower shows p-type conductivity, so the metals are used to form acceptor states in a-Si. The temperature dependence of conductivity allows us to obtain the energy of the levels in the mobility gap for these impurities. In this case the activation energy of conductivity ΔE could be written as $\Delta E = (E_F - E_v) - qT$, where q is a temperature coefficient. We have found the following values of energy levels: $E_v + 0.15$ (Mn), $E_v + 0.18$ (Ni), and $E_v + 0.25$ eV (Fe). It should be noted that the activation energy of conductivity in a-Si:Ni does not change with increasing impurity content by a factor 5 (Fig. 4a). This suggests firstly that the energy levels of defects and Ni in a-Si are superimposed and secondly that direct saturation of dangling bonds with impurities takes place. If dangling bonds disappeared due to the level recharge, the Fermi level would shift up from the defect level by the Hubbard repulsion energy at an increase in the impurity concentration [9].

It is noteworthy that the sample with Fe concentration 10^{19} cm^{-3} behaves as intrinsic material, i.e. the conductivity activation energy is equal to 0.5 eV, the conductivity is $10^{-5}\ \Omega^{-1}$ cm^{-1}, and the thermopower is very small. Thereby we may assume the concentration of Fe close to the density of localized states in order of magnitude.

We now discuss an conduction mechanism of a-Si doped with a transition metal. The semilogarithmic plots of conductivity versus reciprocal temperature over the range 500 to 300 K (Fig. 4 and 5) exhibit constant activation energies. This implies that conduction through the valence band is dominant within this temperature range. The low activation energy (less than 0.04 eV) which appears at $T < 250$ K arises from the hopping conduction through impurity-induced states near the Fermi level. Thermopower and activation energy values decrease with transition metal concentration N above 5×10^{20} cm^{-3} due to the overlapping of the wave functions of the impurity states and impurity band formation.

We have found that the temperature dependence of conductivity for a-Si:Mn with Mn contents of 4, 8, and 10 at% followed the activation law $\sigma(T) \sim \exp\left(-(T_0/T)^{1/2}\right)$ (Fig. 6). This behaviour is valid for the hopping mechanism involving the electron–hole interaction, which causes a Coulomb gap Δ in the spectrum of localized states near the Fermi level. The value of $\Delta \sim k/2(T_0T^*)^{1/2}$ [11], where T^* is the temperature starting from which conductivity follows $\sigma \sim \exp\left(-(T_0/T)^{1/2}\right)$. Theory predicts the parameter $T_0 = 1/k(\beta e^2/\varkappa a)$, where β is the numerical constant of 2.8, e the elec-

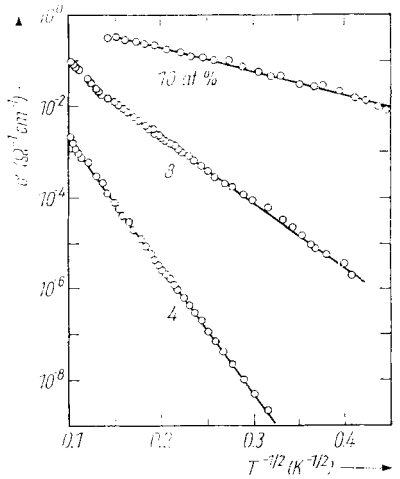

Fig. 6. Conductivity of a-Si films doped with Mn versus $T^{-1/2}$

tron charge, $\varkappa$ the dielectric constant, and a the localization radius [10]. Estimations show that Δ is equal to 25, 10, and 3 meV, respectively, for a-Si:Mn with 4, 8, and 10 at% impurity content. It is substantially higher than for phosphorus-doped a-Si [12]. This result may be explained by the much lower localization length (radius) of states induced by a transition metal atom with nonfilled d-shell. Using again the theory of hopping conductivity [13] we may write the conductivity of the system of randomly dispersed sites as $\sigma \sim \exp(-\zeta/N^{1/3}a)$, where the numerical constant $\zeta \approx \approx 1.7$. From the semilogarithmic plot of conductivity versus reciprocal mean distance between impurity atoms with concentration in the range of 10^{19} to 10^{20} cm^{-3} we obtained the value of $a \approx 1$ nm. In the case of phosphorus-implanted a-Si the localization radius appears to be 10 to 20 nm within the same concentration range.

With increase in impurity concentration the gap tends to zero because of the transition of doped a-Si layers to the quasimetallic state, which was observed by us at 12 and 16 at% of Mn, where the conductivity depends on temperature as $\sigma \sim T^{0.45 \text{ to } 0.8}$.

4. Conclusions

The elements of the first transition row of the periodical table being implanted in a-Si are incorporated into the structural network of the material and form acceptor-type centres. This is accompanied by dangling bond passivation. From the temperature dependence of conductivity three different types of conduction are distinguished. Above 500 K transport via conduction band electrons occurs, within the range 300 to 500 K valence band transport dominates by holes excited from impurity acceptor states, and below 250 K hopping conduction through an impurity band near the Fermi level becomes predominant. In the temperature dependence of the conductivity we observed the occurrence of an energy gap centred at the Fermi energy. The appearance of this gap probably is caused by the Coulomb interaction between carriers at localized states. The maximal width of the gap was anomalously high (25 meV), significantly larger than in phosphorus-doped a-Si.

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