HOT-PROBE METHOD FOR EVALUATION OF MAJORITY CHARGED CARRIERS CONCENTRATION IN SEMICONDUCTOR THIN FILMS

Alexander Axelevitch[1], Gady Golan[1,2]

[1]Holon Institute of Technology (HIT), 52 Golomb St., Holon 5810201, Israel
[2]Ort Hermelin Academic College, 2 Hamehkar St., Netanya 4250401, Israel

Abstract. *Physical properties of thin films significantly differ from those of bulk materials. Also, these properties are influenced from the technological parameters of the films deposition technique. Therefore, characterization methods for evaluation of thin film properties become of high importance. A novel approach to the well-known "Hot-Probe" method is proposed and applied in our work. The conventional Hot Probe characterization method enables only the definition of a semiconductor type, P or N, by identifying the majority of the charged carriers. According to the new Hot Probe technique, one can measure and calculate the impurities concentration and charged carriers dynamic parameters. Feasibility proof of the upgraded Hot Probe method was done in Si and Ge bulk, and in thin film semiconductor samples of In_2O_3 and VO_2.*

Key words: *hot-probe method, semiconductors thin films, semiconductor oxides, charged carriers concentration*

1. INTRODUCTION

There are various parameters such as a thickness, crystal structure, composition and other, which characterize a semiconductor film. However, the parameters of charge carriers define the possibility to apply material for various electronic devices. Specifically, these parameters are as follows:

- Type of semiconductor,
- Impurities concentration,
- Mobility of charged carriers,
- Diffusion coefficient.

Evidently, these parameters are known for crystalline semiconductors and may be measured using conventional methods. Such methods like the "four point probe" and the "Van Der Pauw", enable measurements of sheet resistance. Hall Effect measurements provides data on the majority carrier's mobility and the majority carrier's concentration.

There is no verb in this sentence A Haynes-Shockley experiment provides data on the minority carrier's mobility and the diffusion coefficient. The main problems in application of these methods to thin films parameters measurement are in the measuring device sensitivity and in the complexity of specific samples preparation. Samples for Hall Effect measurement require high precision electrodes arrangement. Haynes-Shockley experiment necessitates specific equipment with short switching time: an electrical pulse generator or a pulse laser for minority carrier's excitation. Thus, these methods cannot be applied for fast evaluation of thin films. The main requirements for evaluation methods are: simplicity, efficiency, and sufficient accuracy.

A conventional Hot-Probe experiment enables a simple and efficient way to distinguish between n-type and p-type semiconductors using a hot probe and a standard multimeter. A principle schematic of the experiment is shown in figure 1 [1].
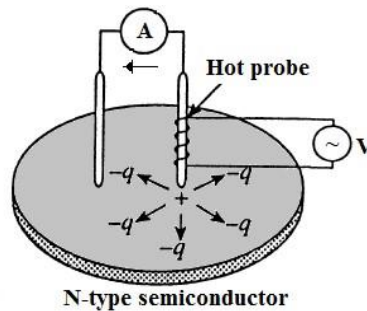

Fig. 1 Principle measurement schematic of Hot-probe experiment

Here, a couple of a cold probe and a hot probe are attached to the semiconductor surface. The hot probe is connected to the positive terminal of the multimeter while the cold probe is connected to the negative terminal. While applying the cold and hot probes to an n-type semiconductor, positive voltage readout is obtained in the meter, whereas for a p-type semiconductor, negative voltage is obtained. An explanation of this experiment is that the thermally excited majority free charged carriers are translated within the semiconductor from the hot probe to the cold probe. The mechanism for this motion within the semiconductor is of a diffusion type since the material is uniformly doped due to the constant heating in the hot probe contact. These translated majority carriers define the electrical potential sign of the measured current in the multimeter.

This Hot Probe experiment can be extended by the two following ways:

1. To connect two cold electrodes to the sample under evaluation and heat one of them; this way we obtain information on the type of semiconductor and the thermo-electrical voltage dependence on temperature (thermo-power or Seebeck coefficient).
2. To heat one of the two probes for a pre-defined temperature and attach it to the film surface for a certain time. The cold electrode must be kept attached to the surface constantly. Attachment is maintained until a steady state is obtained. Then the heater is turned off. This way one gets additional information concerning the majority charged carriers concentration and the dynamic parameters of the semiconductor material.

Generally, the Hot-Probe measurement may be described as a three-step process. First, the heated probe excites additional free charged carriers of two types. Second, the hot

majority carriers begin to leave the heated part of the semiconductor surface by a diffusion mechanism. Simultaneously, a built-in electrical field is created between the electrodes. Simultaneously, the second (cold) electrode is warmed as well. This warming and the built-in electrical field tend to prevent the diffusion process up to a halt at a steady state. This steady state condition exists until the heated source is switched off. The third process is actually a recombination of the excited additional charged carriers. This three-step process may be described, in general, by the continuity and Poisson's equations [2]:

$$\begin{cases} \nabla J + \dfrac{\partial Q}{\partial t} = 0 \\ \nabla E = \dfrac{Q}{\varepsilon_0 \varepsilon_r} \end{cases} \tag{1}$$

Here Q is the uncompensated charge density excited by the heated electrode, J is the current density, ε_0 and ε_r are the absolute and relative permittivity, and E is the built-in electrical field.

It is well known that conductivity behavior in semiconductors shows that the product of positive and negative charged carrier's concentrations p and n, has influence on the temperature according to the following relation:

$$\sqrt{np} = n_{iT} = AT^{\frac{3}{2}} \exp\left(-\frac{E_g}{2kT}\right) \tag{2}$$

where A is the proportionality coefficient depending on the effective mass of charged carriers, E_g is a bandgap of the semiconductor, and k is the Boltzmann's constant. A parameter n_{iT} characterizes the intrinsic charged carrier's concentration for the given temperature [3], [4].

Prior to heating (the steady state), the semiconductor sample is in a compensated electro-neutral state, according to the electro-neutrality rule:

$$n + N_A = p + N_D \tag{3}$$

where N_A is the concentration of acceptor ions and N_D is the concentration of donor ions. In the case of extrinsic semiconductor, a p-type, for example, the N_D value may be neglected and using the charge conservation law ($pn = n_i^2$), equation (3) transforms to:

$$p = n + N_A = n_i^2/p + N_A \tag{4}$$

where $n_i = p_i$ is the intrinsic charged carriers concentration at normal temperature (300 K).

A solution of this equation is:

$$p = \frac{N_A}{2} \pm \sqrt{\left(\frac{N_A}{2}\right)^2 + n_i^2} \tag{5}$$

At higher temperatures, the majority carrier concentration will be changed in Δp that is resulted due to thermal excitation. These additional charged carriers together with the heated majority carriers diffuse from the heated electrode areas to all directions resulting in voltage difference. The approximate solution for additional charged carrier's concentration with the assumption that the effective mass of the charged carriers and the semiconductor bandgap are stable at the temperature variation from room temperature of up to about 150°C, was obtained in the follows form [5]:

$$\Delta p \approx \frac{n_i^2 R^2}{N_A} \tag{6}$$

where

$$R = \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \exp\left[\frac{E_g}{2kT_0}\left(1 - \frac{T_0}{T}\right)\right] \tag{7}$$

And $(T - T_0)$ is the heating temperature.

Equation (6) enables an approximate estimation of the impurities concentration in the semiconductor, or thin film, if measured the additional charge Q. This estimation may be verified by an independent measurement of the material resistivity. The main goal of our work was to prove the proposed theory for thin film coatings of semiconductor oxides such as In_2O_3 and VO_2.

2. EXPERIMENTAL DETAILS

To verify the degree of dependence of the measurement results from a cold electrode heating, we measured simultaneously the temperatures of both the hot electrode and the cold electrode, by independent thermo-couple temperature sensors. Figure 2 presents the obtained temperature characteristics of the cold electrode in various processing time slots.
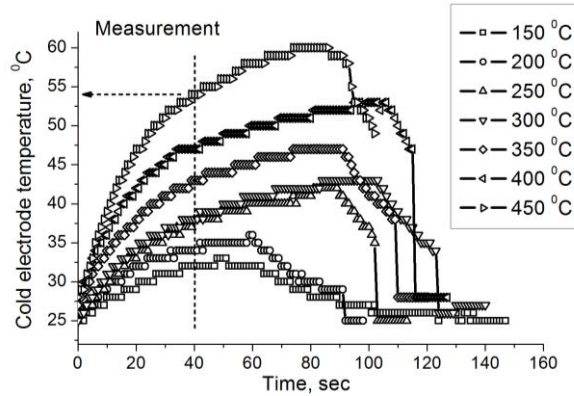

Fig. 2 Cold electrode temperature while measurement

It can be seen that maximum temperature at the second electrode (cold probe) after ~ 40 seconds has not exceeded more than 30°C, for the highest possible temperature of the hot electrode (450°C). In lower temperatures, this difference was smaller and for 150°C on the hot electrode the cold probe temperature was no more than 10°C. Generally, the maximal variation of the cold point temperature was no more than 6.7 % from the hot-probe temperature. Therefore, we may neglect the second electrode heating effect.

Figure 3 presents a hot probe characteristic family of curves, measured in a bulk crystalline germanium sample for various temperatures of the hot electrode. These curves demonstrate positive voltage measured between the two electrodes. Therefore we conclude that the majority

carriers in the Ge sample under evaluation are electrons. In other words, this is an n-type semi-conductor. The temperature influence on the obtained curves was found as follows: by increasing the hot-probe temperature, the measured voltage between electrodes was also increased. All curves were similar to each other. Three different regions may be distinguished in the obtained characteristics: a) a steep rise at the first part, b) fast decrease to a steady state which continues decreasing slowly, and c) a sharp decrease after removing the heater from the electrode. The slope of voltage decrease in the middle part of the curves is influenced by the cold electrode temperature increase due to the high thermal conductivity of the Germanium crystalline. It is interesting to note that the initial growth and the final decay have the same slopes. This indicates an identity of both physical processes of generation and recombination of the charged carriers.

Figure 4 presents an initial part of the Hot-probe characteristic for a germanium crystalline, measured at 150°C. This figure demonstrates the relationship between the initial state and the steady state. The charged carrier's concentration of the germanium sample was estimated using this characteristic.
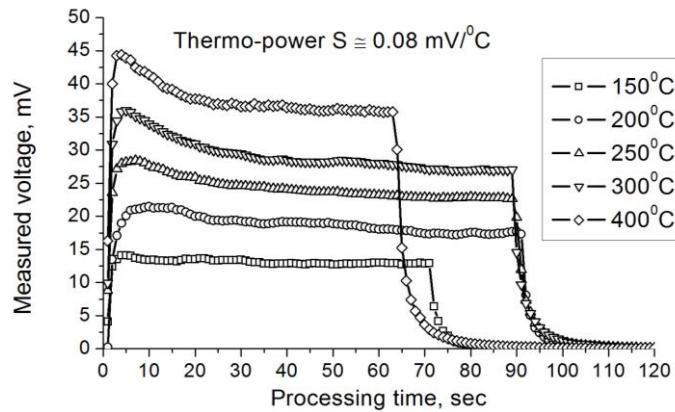

Fig. 3 Hot-probe characteristics for n-type germanium bulk sample in various temperatures
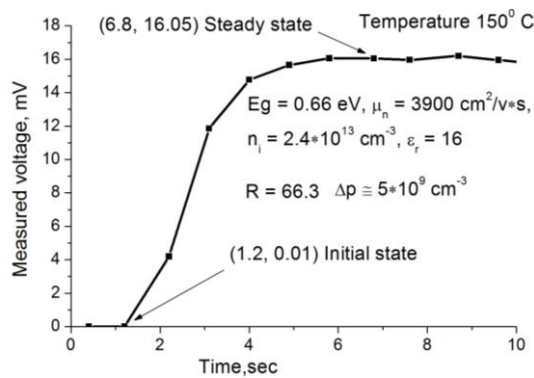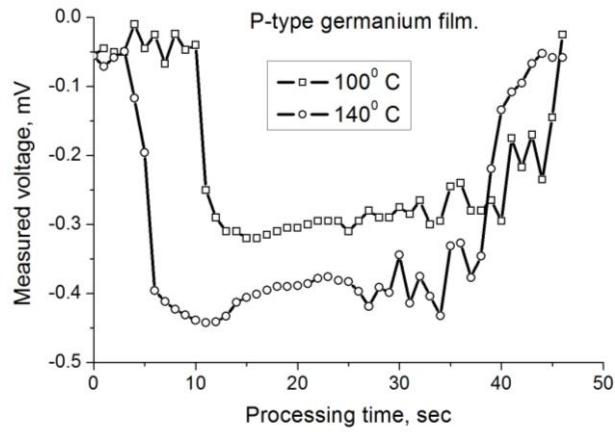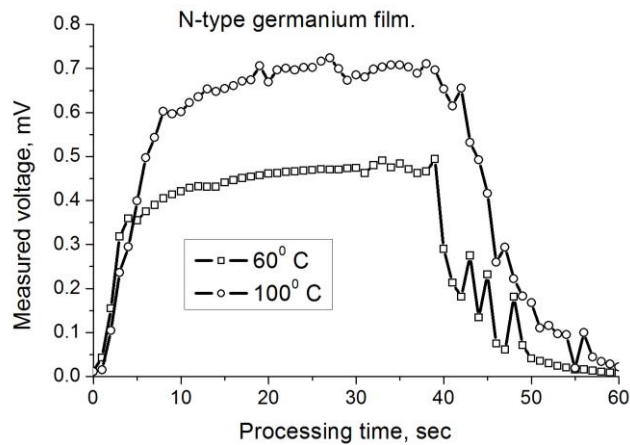

Fig. 4 Hot-probe characteristic of germanium bulk sample, measured at 150°C

Hot-probe characteristics for germanium thin films on glass substrates are presented in figure 5.

(a)

(b)

Fig. 5 Hot-probe characteristics of germanium thin films doped with aluminum during
deposition on glass substrates: (a) P-type film, (b) N-type film

These characteristics present the measured voltages as functions of heating time for
two different temperatures, and show the same behavior of a semiconductor, regardless of
its type. The obtained semiconductor films are of p-type and n-type as shown from the
negative (a) and positive (b) values of the measured voltages. Increasing the aluminum in
the precursor evaporating material, changes the sign of the majority charge carriers in the
grown germanium film. Figure 6 presents the Hot-probe characteristic of indium oxide
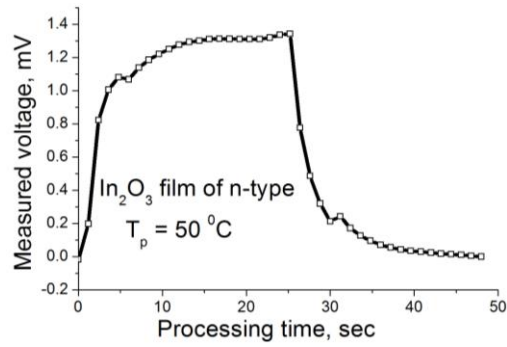thin film.

Fig. 6 Hot-probe characteristics of sputtered indium oxide thin films
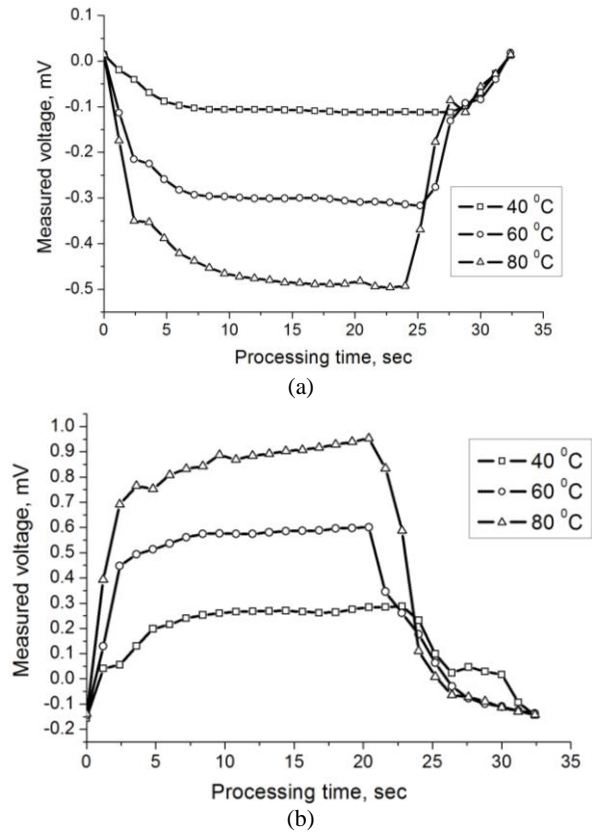

(a)

(b)

Fig. 7 Hot-probe characteristics for vanadium oxide thin films deposited
on the oxidized silicon surface by thermal evaporation:
(a) as-deposited film of P-type, (b) thermally treated film of N-type

This film presents conductivity of n-type which agrees with literature. Vanadium oxide
thin films of p- and n-types are presented in figure 7. The deposited samples were of p-

type. Part of the samples was thermally treated at temperature of approximately 500°C in air. This annealing process results in a change in the conductivity type, as shown in the characteristic (see figure 7-b) [6].

Comparing hot-probe characteristics measured for bulk, and thin film semiconductor materials demonstrates that these materials behave in the same way irrespective of their crystal structure and/or thicknesses. Thus, the same measurement and calculation methods may be applied to characterize thin semiconductor films, regardless of their growth method.

3. DISCUSSION

Thermally excited charged carriers begin diffusing from the hot probe at all directions meaning half sphere or 2π steradians. This diffusion process obeys the Fick's law. In a constant heating temperature, the diffusion process resembles the diffusion from a defined source. The hot charged carriers leave the heated zone and create a depletion region around the hot probe. Thus, this diffusion process is like the known "Drive-in" diffusion process which may be described using the well-known Gauss distribution [7]:

$$N(x,t) = \frac{Q}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{8}$$

where $N(x,t)$ is the concentration of the free charged carriers in distance x and time t and D is the diffusion coefficient of the majority charged carriers. Now, using the relation $Q = qN(x,t)$ the Poisson's equation (1) takes the following form:

$$\frac{\partial E}{\partial x} = \frac{q}{2\pi\varepsilon_0\varepsilon_r} \frac{Q}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{9}$$

This equation may be approximately solved for a voltage drop measured between the hot and cold electrodes in the steady state. After neglecting all of the small components and re-substitution, we obtain the following expression:

$$V = -\frac{q}{2\pi\varepsilon_0\varepsilon_r} \frac{Q}{\sqrt{\pi}} \frac{x^2}{4Dt} \tag{10}$$

The additional charge generated by heating may be obtained from this equation for $x = L$ (the distance between electrodes):

$$Q = -\frac{V \cdot 2\pi^{3/2}\varepsilon_0\varepsilon r \cdot 4Dt}{qL^2} \tag{11}$$

In the first approximation, the diffusion coefficient value may be calculated using the well-known Einstein equation and tabular value of the charged carrier's mobility for a given temperature. The sign of Δp is defined by the type of material. Calculations according to formulae (6) and (11) will obtain the majority of the charged carriers concentration.

The type of semiconductor material is defined in the conventional "Hot-Probe" method by the sign of the measured voltage. A thermo-electric power (Seebeck's coefficient) may be calculated from measurements of the voltage at various temperatures. For example, in order to build the relationship of thermoelectric power and temperature,

we use figure 3. Maximum value of the voltage should be related to the temperature. The angle of slope of the graphical characteristics is equal to the thermoelectric power. To estimate the majority charged carriers concentration, (6), (7) and (11) should be used.

Estimation of the majority charged curriers was done for Ge sample, n-type. Their hot-probe characteristic is presented in figure 4. As shown, the sample was measured by hot-probe at 150^0C. The time interval between the initial state and steady state was of 5.6 sec, and the maximal measured voltage was 16.04 mV. Additional data for the Ge sample were taken from ref. [7]: E_g = 0.66 eV, μ_n = 3900 cm^2/v·s, n_i = 2.4·10^{13} cm^{-3}, ε_r = 16. Calculation was obtained the following values: R = 66.3, $\Delta p \approx$ 5·10^9 cm^{-3}, and $N_D \approx$ 2.5·10^{21} cm^{-3}, which agrees with a direct resistivity measurement.

4. CONCLUSION

- A novel approach to the well-known hot-probe method was proposed.
- The novel approach consists of measurement of the thermo-generated voltage between heated and cold electrodes along a heating and relaxation periodic cycle.
- Estimation of the majority charged carriers concentration is done for a germanium sample and agrees with the conventional measurements.

REFERENCES

[1] A. Bar-Lev, G. Golan, "*Semiconductors*", The Open University of Israel 20402, Tel-Aviv, Israel, 1996 (Hebrew).

[2] I. N. Volovichev, Yu. G. Gurevich, "*Generation–Recombination Processes in Semiconductors Semiconductors*", vol. 35 (3), pp. 306-315, 2001.

[3] S. O. Kasap, "Principle of Electrical Engineering Materials and Devices", McGraw Hill, Boston, 1997.

[4] "*Solid State Physics*", edited by A.F. Khokhlov, The Higher School, Moscow, 2001 (Russian).

[5] G. Golan, A. Axelevitch, B. Gorenstein and V. Manevych, "*Hot-Probe Method for evaluation of impurities concentration in semiconductors*", Microelectronics J., vol. 37, pp. 910-915, 2006.

[6] A. Axelevitch, B. Gorenstein, G. Golan, "*Preparation and investigation of VO$_x$ thin films of n- and p-types*", Thin Solid Films, vol. 515, pp. 8446-8449, 2007.

[7] S. A. Campbell, "The Science and Engineering of Microelectronic Fabrication", Oxford University Press, NY, 2001.