SOVIET PHYSICS JETP VOLUME 32, NUMBER 2 FEBRUARY, 1971

THE SLOWING DOWN OF LOW ENERGY PROTONS IN FILMS OF SiO_2

G. A. ZHUKOVA, V. S. KEESEL'MAN, V. N. MORDKOVICH, and G. F. ZABOTINA

Submitted March 5, 1970

Zh. Eksp. Teor. Fiz. 59, 414–418 (August, 1970)

A technique is described for determining the range of charged particles in dielectric targets, based on deposition of dielectric films on the surface of semiconducting plates and study of the changes in the characteristics of the dielectric-semiconductor system under bombardment. An investigation has been made of the slowing down of 15–50 keV protons in SiO_2 films, and values of the mean and maximum ranges have been obtained. The experimental results are compared with the theory of Lindhard.

THE usual methods of determining the range of nuclear particles are based on bombardment of foils of various thicknesses, prepared from the material being investigated, and measurement of the number of particles which have passed through the foil and reach a detector located byond it.[1] Naturally, for very low-energy particles, whose ranges are small, these methods are very difficult in practice, since it is a rather difficult problem to obtain uniform and mechanically stable foils 10^2–10^3 Å thick. This fact evidently also explains the relatively small amount of experimental data which have been published up to this time on slowing down of low energy protons in matter. Studies of the ionization loss of protons in monatomic metals and semiconductors are well known (see, for example, the work of Arkhipov and Gott[2]). At the same time, practically no work has been done so far on the study of energy losses of such particles in dielectrics, in binary compounds, and in more complicated compounds (Makarov and Petrov[2] have succeeded in establishing only the maximum range of protons in silicon carbide, and Hines[4] has determined the median range of the particles in quartz, but this has been done by an indirect method). However, it appears to us that there is undoubted interest in investigation of the slowing down of protons in dielectrics and materials of complex composition and in comparison of the experimental results with theoretical predictions.

The present work is devoted to study of the slowing down of low-energy protons (15–50 keV) in the binary dielectric silicon dioxide. For this purpose we have developed a new method of determining the ranges of particles, which is free from the limitations mentioned above.

DETERMINATION OF PROTON RANGE

The means used in the present work to study the slowing down of protons is based on the deposition of thin films of the material under investigation on the surface of a semiconducting substrate, bombardment of the structure obtained, from the dielectric side, and study of the changes in the electrical characteristics of the dielectric-semiconductor boundary as the result of radiation damage. As characteristics to investigate we have chosen the charge Q of the dielectric-semiconductor boundary and the surface recombination rate S in the semiconductor.

It is evident that changes in the parameters of the semiconductor or of the boundary will occur if the condition $d \leq R$ is satisfied, where d is the dielectric thickness and R is the range of the particle, and for $d > R$ the values of Q and S will remain constant.

The transition, in a plot of Q or S as a function of the dielectric thickness, from the constant portion to the variable part at smaller d values permits determination of the maximum value of the range R_{max}. Information of this type is important, for example, in the physics and technology of semiconductors, since in preparation of semiconductor devices by the ion-implantation method, it is usual to bombard a crystal whose surface is covered with a dielectric film.

On the other hand, the maximum change of Q under the influence of bombardment corresponds to the case in which the greatest number of particles is stopped directly at the dielectric-semiconductor boundary.[5] Therefore, the extremum point in the experimental function $Q = f(d)$ obtained for a constant energy of bombarding particle corresponds to the condition $d = \overline{R}$, where $\overline{R}$ is the mean range of particles of the given energy.[1)]

EXPERIMENTAL METHOD

SiO_2 films of various thicknesses were deposited on the surface of polished silicon plates by means of the pyrolytic reaction, oxidation of $SiCl_4$ in the presence of CO_2 in a flux of hydrogen at a temperature of 1200°C.[6] The film thickness was varied over the range 1000–9000 Å, and the uniformity in thickness over each sample was better than ± 50 Å. The samples were bombarded by protons, after which structures of the type metal-SiO_2-Si-metal were prepared (by evaporation at room temperature of Al on the entire Si surface and of nine contacts of Al 0.5 mm in diameter on the surface of the oxide), and the capacitance of

---

[1)] The method described can be used to measure the ranges of particles not only in dielectrics, but also in conducting materials (metals and semiconductors). For this purpose it is necessary to deposit on the semiconducting substrate a thin (in comparison with the expected value of range) intermediate layer of dielectric, and on top of the dielectric—a film of the material under study. The range can be conveniently determined from the dependence of Q on the total thickness of the covering $d = d_x + d_1$, where d_x is the target thickness, and d_1 is the thickness of the intermediate dielectric film. The error in determination of the range will obviously be smaller if d_1 is smaller.

the structure obtained was measured as a function of the applied dc voltage.

The charge of the dielectric-semiconductor boundary Q can easily be calculated from the experimental C-V characteristic.[7] A block diagram of the measuring equipment and a view of the structure investigated are shown in Fig. 1. The measurements were made at a frequency of 5 MHz at nine points of each sample by a single-probe method which allowed any of the contacts located on the oxide to be connected to the input of the measuring system. In this way we obtained the value of Q as a function of the dielectric thickness d, and from these values we determined the mean and maximum ranges of protons of various energies. A characteristic experimental curve is shown in Fig. 2.

The maximum range of protons in the dielectric films was determined also by measuring the rate of surface recombination S of silicon covered by a SiO_2 film. For this purpose we cut out of the oxidized plates samples 12 × 5 mm in size, from whose ends the oxide was removed, and at these places we made ohmic contacts by chemical deposition of nickel. Measurements of S before and after bombardment were made by the stationary photoconductivity method[8] with surface generation of charge carriers by light of wavelength 0.4–0.6 microns. A block diagram of the equipment and a view of the sample are shown in Fig. 3, and a typical experimental result in Fig. 4.

In some cases we also varied the means of formation of SiO_2 on the silicon surface. Thermal oxidation and pyrolytic decomposition of tetraethoxysilane[6] were used, without any effect on the results within experimental error. The bombardment was performed by protons with energies from 15 to 50 keV. The particle dose was 10^{13}–10^{14} per cm^2, the proton current in the beam 1–10 μA, and the sample temperature not above 40°C.

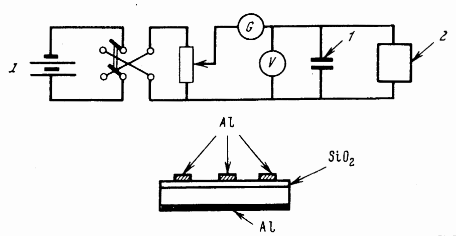

FIG. 1. a–Block diagram of equipment for measuring C-V characteristic of Si-SiO_2 structures: 1–structure being measured, 2–capacitance-measuring device; b–appearance of structure being measured.

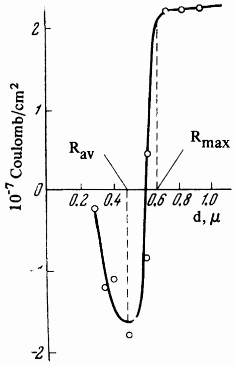

FIG. 2. Experimental curve of charge of the boundary of Si-SiO_2 structures bombarded by 50-keV protons, for various dielectric thicknesses. R_{av} is the mean range of the protons, and R_{max} is the maximum range.

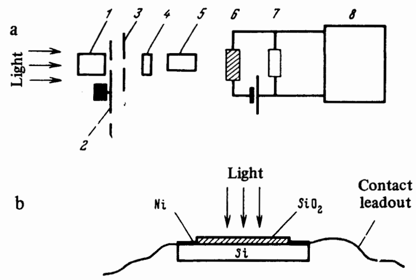

FIG. 3

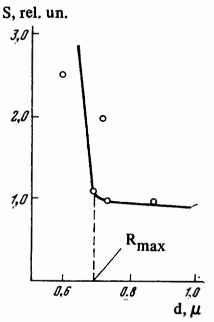

FIG. 4

FIG. 3. a–Block diagram of equipment for measuring surface recombination rate: 1–condensing lens, 2–mechanical modulator, 3–slit, 4–optical filter which assures surface generation of carriers in Si, 5–objective, 6–sample, 7–load resistance, 8–amplifier; b–appearance of sample being measured.

FIG. 4. Experimental dependence of surface recombination rate in Si-SiO_2 structures bombarded by protons, for various dielectric thicknesses. Proton energy 50 keV. R_{max} is the maximum proton range.

RESULTS AND DISCUSSION

The results of the experiments in which the mean and maximum ranges of 15–50 keV protons were determined are shown in the table, where we have also shown the range values obtained from the theory of Lindhard, Scharff, and Schiott[9] (the LSS theory). The LSS theory can be used for ions whose energy $E \lesssim E_1 = 25Z_1^{4/3}A_1(\text{keV})$, where Z_1 and A_1 are the atomic number and mass number of the ion. In the case of protons this corresponds to 25 keV. The proton ranges were calculated with inclusion of the effect of multiple scattering, i.e., the table gives the so-called "projected ranges."[10] In accordance with ref. 9, in calculation of the mean range in the binary compound SiO_2 we performed the averaging according to the equation

$$\bar{R}_{a,b} = \frac{\bar{R}_a \bar{R}_b}{\varkappa_a \bar{R}_a + (1-\varkappa_a)\bar{R}_b},$$

where $\bar{R}_a$ and $\bar{R}_b$ are the ranges of ions in the monatomic materials, $\mathscr{K}_a$ and $1 - \mathscr{K}_a$ are the relative quantities of the elements a and b (in our case $R_a = R_{Si}$, and $\mathscr{K}_a = 1/3$). As a result of the fact that in this case the asymmetry of the range distribution curves for the ions is small (the theoretical values of the

Experimental and theoretical values of proton range in SiO_2

E, keV	R_{max}, μ	R, μ	R_{theor}, [9], μ	Sk_ρ *
15	0,33	0.17	0.21 ±0.03	–0.81
25	0.48	0,25	0.30 ±0.04	–0.95
30	0.55	0.28	–	–
40	0.58	0,33	–	–
50	0.66	0,48	–	–

*Asymmetry coefficient $SK_\rho = \overline{\Delta R^3}/[\overline{\Delta R^2}]^{3/2}$, where $\overline{\Delta R^2} = \overline{(R - R)^2}$, $\overline{\Delta R^3} = \overline{(R - \bar{R})^3}$ are the second and third central moments of the proton range distribution.

asymmetry coefficient Sk_ρ obtained on the basis of ref. 11 are shown in the table) and the curves are rather narrow (the calculated values of the square root of the half-width of the range distribution curve are shown in the table and in the graph of theoretical range values), in this work we made no distinction between average and most probable ranges.

In conclusion it should be mentioned that in this energy region the number of radiation defects arising as the result of proton bombardment is considerably larger than would be produced, according to estimates, by protons which have lost an energy equal to the theoretical value in elastic collisions. At the present time, experimental studies are being made in order to clarify the possible causes of production of defects in the structure on bombardment of semiconductors and dielectrics by low-energy ions.

---

[1] S. V. Starodubtsev and A. M. Romanov, Prokhozhdenie zaryazhennykh chastits cherez veshchestvo (Passage of Charged Particles Through Matter), Academy of Sciences, Uzbek S.S.R., Tashkent, 1962.

[2] E. P. Arkhipov and Yu. V. Gott, Zh. Eksp. Teor. Fiz. 56, 1146 (1969) [Sov. Phys.-JETP 29, 615 (1969)].

[3] V. V. Makarov and N. N. Petrov, Fiz. Tverd. Tela 8, 3723 (1966) [Sov. Phys. Solid State 8, 2993 (1967)].

[4] R. L. Hines, Phys. Rev. 120, 1626 (1960).

[5] M. Simons, L. Monteith, and J. Hauser, IEEE, Trans. Electron Devices, ED-15, 966 (1968).

[6] Basic Technology of Silicon Integrated Circuits. Oxidation, Diffusion, and Epitaxis. Edited by R. Burger and R. Donovan, (Russ. translation), Mir, 1969.

[7] D. R. Kerr, IBM J. Res. Develop. 8, 385 (1964).

[8] S. M. Ryvkin, Fotoelektricheskie yavleniya v poluprovodnikakh (Photoelectric Phenomena in Semiconductors), Fizmatgiz, 1963.

[9] J. Lindhard, M. Scharff, and H. Schiott, Mat. Fys. Medd. Kgl. Dan. Vid. Selsk. 33, No. 14, (1963).

[10] V. S. Kessel'man, Fizika i Tekhnika Poluprovodnikov (Soviet Phys.-Semiconductors) 4, 228 (1970).

[11] V. S. Kessel'man, Fizika i Tekhnika Poluprovodnikov (Soviet Phys.-Semiconductors) 4, 1202 (1970).

Translated by C. S. Robinson
48