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Two-Band Conduction of Amorphous Silicon Nitride

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A method is proposed for determining the electron and hole components of stationary current flowing through an MIS structure and the hole and electron components of the stationary current in an MNOS structure have been determined. It is shown that the experimental results may be explained by a two-band Si_3N_4 conduction model. A two-band Si_3N_4 impurity conduction model with silicon microcrystals is examined, the latter serving as Poole-Frenkel centres in the nitride volume as well as trapping and recombination centres in the regions close to the electrodes.

В работе предложен метод определения электронной и дырочной компонент стационарного тока через МДП-структуру. Определены дырочная и электронная компоненты стационарного тока, возникающего в сильном электрическом поле в МНОП-структуре. Показано, что экспериментальные результаты могут быть объяснены с помощью двузонной модели проводимости Si_3N_4. Рассматриется модель двузонной примесной проводимости Si_3N_4 с микрокристаллами кремния, служащими центрами Пула-Френкеля в объёме нитрида и центрами захвата и рекомбинации в приэлектродных областях.

1. Introduction

The conduction of an amorphous silicon nitride film in MNOS structures with a tunnelable thin oxide layer has been studied in [1, 2]. According to these papers all the experimental data can be explained by a single-band conduction model for Si_3N_4 and a recombination of charge carriers in the SiO_2–Si_3N_4 interface. The question about the current transport band in the nitride or the participation of each band in conduction has so far been left open.

Recently Kobayashi and Ohta [3] have obtained experimental data confirming the electronic nature of Si_3N_4 conduction. We have recently detected [1] a symmetry in the current–voltage characteristic of MNS structures with p- and n-substrates; therefore, it is possible to assume the existence of a certain symmetry in the conduction of Si_3N_4 and its bands. In order to obtain data on the nature of the conduction in the amorphous Si_3N_4 and SiO_2–Si_3N_4 system, we have carried out the following investigation. An experimental method has been developed for the determination of electron and hole current components in the Si–SiO_2 interface of MNOS structures. This allows to determine the sign of charge carriers in systems where the measurement of Hall effect or thermopower presents some difficulty (particularly in MIS systems). Quantitative data on Si_2–SiO_2 interface electron and hole currents in MNOS structures were obtained. It has been concluded that both holes and electrons take part in conduction in silicon nitride.

2. Method of Current Separation

A transistor circuit for the examination of the current flowing through an MNOS structure with a blocking SiO_2 layer over source and drain is shown in Fig. 1. The samples have been made using conventional planar technology: p-channel transistors using n-silicon (100) with 7.5 Ωcm resistivity and n-channel transistors (100) with 0.5 Ωcm resistivity. A lower-resistance substrate was used when making the n-channel device to exclude a shunting inversion layer under the masking oxide. The 20 Å superthin oxide film was grown under control at 700 °K in a dry oxygen flow. The 1000 Å nitride was deposited in a vertical reactor by the tetrachloride or monosilane process in a hydrogen flow at 850 °K. A p-channel transistor circuit for the separation of electron and hole currents of MNOS structures in a silicon substrate inversion mode is shown in Fig. 1. The reverse-bias p–n junction current in the samples used was less than 10^{-10} A at 15 V. We consider the separation principle of electron and hole current components. The discussion remains true for an n-channel transistor when we change the signs of voltage and charge carriers. When voltage is applied to the gate of the structure the gate current is determined by the current through the silicon nitride layer covering solely the superthin oxide. The MNOS current–voltage characteristic is shifted towards higher voltages by the 1000 Å blocking oxide underlayer. Negative voltage forms an inversion p-channel on the silicon surface. The carrier concentration in the channel is determined solely by the field magnitude in the dielectric. It does not depend on the hole current flowing from the silicon into the dielectric inasmuch as the excess holes on the surface are provided by a supplementary carrier flow from the p^+ regions.

The gate current j_g is composed of the electron current injected into the silicon band and of the hole current drawn out of the inversion layer into the dielectric:

$$j_g = j_g^e + j_g^h \,.$$

The hole current from the inversion layer into the dielectric is due to carriers arising from anomalous generation in the space charge region [1] as well as carriers induced from the p^+ regions:

$$j_g^h = j_R^h + j_{p-n}^h \,.$$

The current in the substrate circuit is equal to the sum of two components: carriers injected into the silicon from the dielectric and the electron component of the anomalous generation current:

$$j_s = j_g^e + j_R^e \,.$$

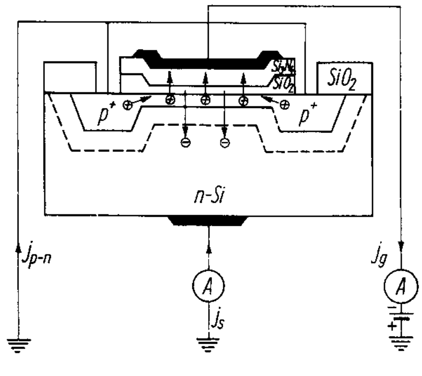

Fig. 1. p-channel test transistor circuit

Thus, the currents are

$$j_s = j_g^e + j_R^e; \quad j_g = j_g^e + j_R^h + j_{p-n}^h \,.$$

If the conduction in the nitride is caused by electron motion through the conduction band then an electron injection current from the dielectric into the n-silicon different from zero may reasonably be expected, i.e. the substrate current in the p-channel transistor must differ from j_R^e the main features of which are described in [1].

The conduction of silicon nitride may also be due to hole motion in the valence band. In this case a non-zero injection hole current j_g^h from the dielectric into the p-silicon may be expected; i.e. the substrate current in the n-channel transistor is different from j_R^h.

3. Results and Discussion

Fig. 2 shows typical experimental results for p- and n-channel nitride structures obtained by the silicon tetrachloride ammonia process. The experimental points for the total current show good agreement with lines plotted according to the Poole-Frenkel law. The $j_s = f(\sqrt{F})$ dependence being as a rule non-linear, the substrate current increases faster than j_g when the gate voltage increases.

It follows from the above that

1. j_s is low in comparison with j_g, but is high compared to the anomalous generation current, and their electric field dependences differ;
2. absolute values and electric field dependence of p- and n-substrate currents are almost equal.

The $j_s = f(F)$ dependence and the p- and n-substrate current ratio are nearly equal for silane and silicon tetrachloride synthesized nitrides.

The fact that j_s is small compared with j_g leads to the following conclusion: The basic current component through the Si–SiS$_2$ interface is due to carriers induced in the inversion channel, i.e. holes in the case of a p-channel and electrons in the case of an n-channel. On the other hand, the $j_s = f(E)$ current is considerably higher than the maximum current due to anomalous generation. This points to the fact that it is due to injection from the dielectric. Thus the j_s component in a p-channel transistor is caused by electron injection and in an n-channel transistor by hole injection.

In principle electrons can be injected into the silicon conduction band both from the conduction (j_d') and valence (j_d'') bands of Si$_3$N$_4$ (Fig. 3a). However, the electron injection from the Si$_3$N$_4$ valence band into the silicon conduction band (p-channel transistor) can be neglected as compared to the injection from the Si$_3$N$_4$ conduction band. The reason is that the barrier values for such tunneling junctions differ considerably. An identical situation takes place in an n-channel transistor where holes from the Si$_3$N$_4$ valence band are injected.

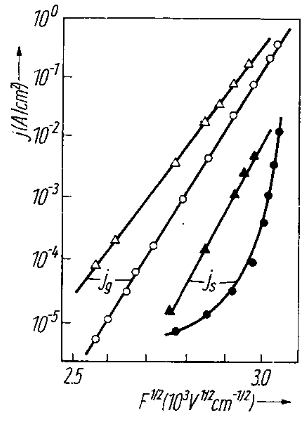

Fig. 2. Gate (j_g) and substrate (j_s) current versus average nitride field value in p- and n-channel transistors with a tunnelable thin SiO$_2$ layer. ○, ● —Al, n-Si; △, ▲ +Al, p-Si

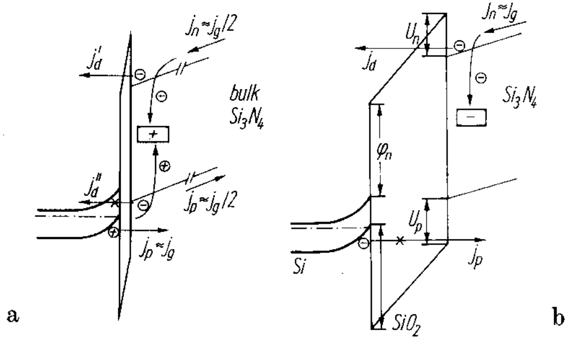

Fig. 3. Energy diagram of a a) tunnelable and an b) untunnelable oxide layer MNOS capacitor

When the SiO_2 layer thickness in a p-channel structure is increased to 200 Å, $j_{\text{p-n}}$ becomes much lower than j_g and j_s, i.e., practically the whole j_g current is an electron injection current from Si_3N_4 into the silicon conduction band. Such a transformation of the current components can easily be understood as the triangular barrier U_n for electrons is much lower in the case of a thick SiO_2 layer (SiO_2–Si_3N_4) compared to the barrier for holes, U_p (Si–SiO_2) (Fig. 3b). An analogous situation has evidently taken place in n-channel transistors as well.

Fig. 4 shows current–voltage curves of a MNOS capacitor with a 200 Å oxide layer. The difference between these curves and the tunnelable thin oxide layers (1) is easily discernable. First, contrary to the data cited in [3] there is no current saturation neither in n- nor in p-silicon when the exhaustion voltage is applied. This can be explained by the fact that the extraction of minority carriers and the concomitant development of an exhaustion layer in thin oxide MNOS tunnel structures is replaced by the injection of carriers from the dielectric. Secondly, the current–voltage characteristics are not symmetrical as regard polarity change. The current at positive voltage at the metal electrode is lower than at negative voltage. This asymmetry has been observed earlier in [4, 5], but the

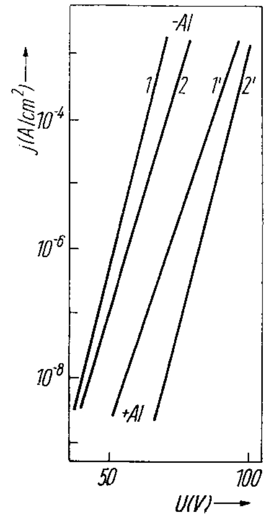

Fig. 4. Current–voltage characteristics of an untunnelable MNOS capacitor. (1,1′) p-Si; (2, 2′) n-Si; $d_{\text{ox}} = 200$ Å, $d_{\text{nitr}} = 800$ Å

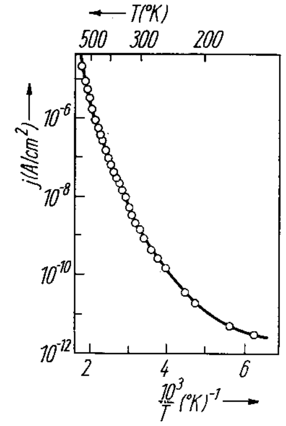

Fig. 5. The temperature dependence of direct current through the MNOS structure with a tunnelable oxide. $S = 5 \times 10^{-3}$ cm²; —Al; $F = 4.13 \times 10^6$ V/cm

asymmetry sign was opposite. According to [4] the current in the MNOS structure with a thick oxide layer is determined by the nitride layer. This is caused by the low barrier values on the SiO_2–Si_3N_4 contact. The current–voltage curve asymmetry is therefore due to the difference in the accumulated charge at the interface, i.e. the electric field value in the nitride.

If the nitride conduction were conditioned only by electron motion [3, 6], then, using negative silicon, a Fowler-Nordheim injection through the oxide should be apparent [7]. The latter must always be lower than the current limited by the nitride volume.

Almost equal values of n- and p-j_s currents in thin oxide MNOS tunnel transistors and lack of j_g current saturation in MNOS capacitors with oxide thickness $\gtrsim 200$ Å may well be explained by a two-band conduction model for the nitride. Different signs of the current–voltage curve asymmetry point to the same assumption.

Two-band conduction of the silicon nitride bulk can be both intrinsic and due to impurities. The temperature dependence of current (Fig. 5) between 250 and 550 °K and the field dependence in the $T < 250$ °K region lead to the conclusion that the free charge source is a continuum of electron states. Apparently, an electric field and temperature increase brings about an increase in the mean excitation energy, becoming apparent in the rising slope of the curve. The effective activation energy Φ'_{eff} determined by the slope according to formulae (1) and the effective barrier Φ''_{eff} (2),

$$j_{\text{P-F}} = j'_0 \exp\left(-\frac{\Phi'_{\text{eff}} - dF^{1/2}}{kT}\right), \tag{1}$$

$$j_{\text{F-N}} = j''_0 \exp\left(-\frac{\beta(\Phi''_{\text{eff}})^{3/2}}{F}\right), \tag{2}$$

varies from 1 to 2 eV.

The transmission of amorphous silicon nitride begins in the neighbourhood of 3 eV (Fig. 6), while the width of the forbidden gap of crystalline nitride is about 4 eV [8]. The reason of this film absorption edge cannot at present be uniquely defined. It is not clear whether it can be due to impurities or density of states tails. Thus, it cannot be exluded that the two-band of the conduction nitride may be intrinsic. So far, however, there is no theoretical model for amorphous dielectric conduction in a high electric field.

We consider, therefore, the experimental data in an impurity conduction model. It is known [9] that silicon nitride conduction rises exponentially with the increase of the SiH_4/NH_3 ratio in the reactor above a certain threshold.

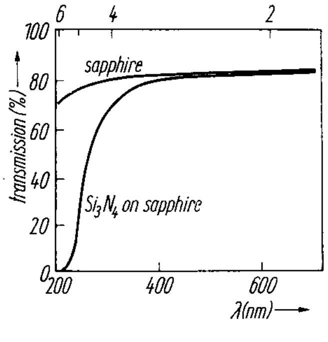

Fig. 6. The transmission spectrum of the silicon nitride film on sapphire. $SiH_4/NH_3 = 0.07$, $d_{\text{nitr}} = 1.70$ μm

This increase may be explained by the fact that the conduction is determined by ionization of silicon microcrystals originating in the Si_3N_4 matrix [10].

The increasing SiH_4 content reduces the average distance between crystallites, leading to a drop in their ionization potential barrier [11]. Such a crystallite ensures two-band impurity conduction in a high electric field by the Poole-Frenkel mechanism. In the absence of an electric field the crystallite is neutral and has neither free holes nor electrons. When an electric field is applied the electron and the hole are released one after the other by the Poole-Frenkel mechanism at high temperatures and by Fowler-Nordheim injection at low temperatures. Thus, both Si_3N_4 bands take part in the stationary conduction, though the electric field acts on the barrier only during the release of electrons.

The charge carrier recombination in the contact regions is also explained by the proposed model. It is known that the hysteresis loop of a tunnelable thin oxide MNOS structure due to carrier capture into the nitride layer near the substrate begins in a lower field region compared with stationary conductance [12]. Thus, the stationary current in Si_3N_4 is accompanied by the electrode polarization. If it is assumed that just the silicon crystallites mentioned above are acting as charge trapping centres, then they must be positively charged near the anode and negatively near the cathode. In steady-state conditions charged crystallites in the close electrode region of an attenuated field will act as recombination centres with a large capture cross-section, thus ensuring the recombination processes cited above.

4. Conclusions

1. In this paper we have proposed a method for separating the current in an MNOS structure into electron and hole components. The method can be applied for the determination of charge carrier signs in MIS structures with any kind of dielectric.

2. It is experimentally shown that the basic current component at the $Si–SiO_2$ interface in tunnelable thin oxide MNOS structures is the carrier current from the semiconductor into the dielectric. The injection current from the dielectric into the silicon is low and the absolute values for p- and n-silicon are nearly equal.

3. In thick oxide MNOS structures the basic component of the $Si–SiO_2$ interface current is the injection current from the dielectric into the silicon.

4. It is shown that experimental data on the stationary conduction in silicon nitride should be interpreted on the basis of a two-band model.

5. A two-band Si_3N_4 impurity high-field conduction model is proposed, in which silicon microcrystals act as Poole-Frenkel and recombination centres.

References

[1] A. S. GINOVKER, V. A. GRITSENKO, and S. P. SINITSA, Theses of Lectures on IV. All-Union Conf. on Electronic Processes at the Surface of Semiconductors, Naukova dumka, Kiev 1971; Phys. Dielectrics and Perspectives of Its Development, All-Union Conf., Leningrad 1973, Vol. III, (p. 31).

[2] A. S. GINOVKER, V. A. GRITSENKO, and S. P. SINITSA, Mikroelektronika **2**, 283 (1973).

[3] K. KOBAYASHI and K. OHTA, Japan. J. appl. Phys. **11**, 538 (1972).

[4] B. SWAROOP and P. SCHAFFER, J. Phys. D **3**, 803 (1970).

[5] B. E. Deal, P. J. Fleming, and P. L. Castro, J. Electrochem. Soc. **115**, 300 (1968).
[6] D. Frohman-Bentchrowsky, Proc. IEEE **58**, 1207 (1970).
[7] M. Lenzlinger and E. H. Show, J. appl. Phys. **40**, 278 (1969).
[8] Yu. N. Volgin, G. P. Dubrovskii, A. M. Zykov, V. P. Kovalev, and Yu. I. Ukhanov, Fiz. Tekh. Poluprov. **4**, 2398 (1970).
[9] G. A. Brown, W. E. Robinette, and H. U. Carlson, J. Electrochem. Soc. **115**, 948 (1968).
[10] M. V. Coleman and D. J. D. Thomas, phys. stat. sol. **25**, 241 (1968).
[11] K. Tanabashi, and K. Kobayashi, Japan. J. appl. Phys. **12**, 641 (1973).
[12] A. S. Ginovker and S. P. Sinitsa, Elektronnaya tekhnika, Ser. 2, 75 (1972).
[13] V. I. Belyi, V. V. Voskoboinikov, A. S. Ginovker, E. A. Krivorotov, and S. P. Sinitsa, Mikroelektronika **1**, 182 (1972).

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