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Title EFFECT OF ETCHES ON SURFACE RECOMBINATION IN SILICON

Abstract Approved (Major Professor)

This thesis presents a limited investigation of the effects of various etches on the surface properties of silicon. Surface recombination velocities of silicon under different etching treatments are compared by using the photoelectromagnetic effect. A measure of the minority carriers lifetime by the photoconductive decay method provides another means of comparing various surface treatments and ambient atmospheres.

CP-4 etch yields the smallest surface recombination velocity in silicon; while sodium dichromate solution has the pronounced effect of reducing the minority carrier lifetimes in silicon. Ambient atmospheres have no obvious influence on the surface recombination velocity of silicon.
THE EFFECT OF ETCHES ON SURFACE RECOMBINATION IN SILICON

by

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EFFECTS OF ETCHING ON SURFACE RECOMBINATION
IN SILICON

INTRODUCTION

The simple band theory for bulk properties of materials is not adequate to predict the behavior of semiconductor properties close to the surface of the semiconductor. In particular the importance of the surface of P-N junctions and transistors was not fully understood until the postulation of surface states in 1947 by Bardeen (1, p. 717). While he was studying rectification of semiconductor, he developed the idea of space charge region at a free surface.

An intensive study has been carried on since on the properties of semiconductor surfaces, especially germanium. It has been found that a density of the surface states, greater than $10^{13}$ per cm$^2$, is high enough to overwhelm the effects of the bulk impurities such that the conductivity at the surface is almost completely controlled by the surface conditions. Likewise, various electrical parameters are found to be affected by the surface conditions in the semiconductors. Statz et al. (13, p. 139) proposed that the leakage current along the surface of a P-N junction in the presence of water vapor can be explained by the hole conduction in the liquid at the boundary between the solid and liquid phases. There may also be conducting layers along the surface which can easily short the emitter to the collector in a grown-junction transistor. Maple and Bess (9, p. 490) found
that $\frac{1}{f}$ noise presented in semiconductors is sensitive to ambient atmosphere. Surface breakdown, explained by Garrett and Brattain (4, p. 299), is induced by the presence of surface charge having the same sign as the body impurity on the high resistivity side of the P-N junction.

Certain electrical parameters, such as the current transfer ratio of a transistor, favor a surface condition which gives little recombination. This thesis presents the results of a limited investigation of the effects of different etches on the surface preparation of silicon. In particular, surface conditions which will render a low surface recombination velocity in silicon were investigated.
MODEL OF A SEMICONDUCTOR SURFACE

Surface Charge

The true semiconductor surface may be observed in crystals which have been cleaned (generally by ion bombardment) in a high vacuum. The existence of a surface layer which has oxygen and, possibly, a few other impurities is always found on a semiconductor surface. This surface layer contains an electrical charge which affects the characteristics of the semiconductor material which is near the surface. The exact mechanism for the existence of this surface charge may be due to absorbed ions and dipolar molecules.

The electrical surface charge may be either positive or negative. To neutralize any charge in the surface layer, the energy bands must bend at the surface so that carrier concentrations are changed to give the required space charge. A negative surface charge is neutralized by a positive charge within the bulk of the material. According to Poisson's equation, a finite electric field exists, and the electric field accounts for the bending of the energy bands at the surface. The energy diagram of a semiconductor surface is illustrated in Figure 1.
Figure 1. Energy Diagram of a Semiconductor Surface

The symbols shown are defined as follows:

\( E_C \) = energy level of bottom of conduction band

\( E_V \) = energy level of top of valence band

\( E_F \) = Fermi level

\( E_i \) = intrinsic Fermi level

\( \psi \) = electrostatic potential

\( q\phi = E_F + q\psi \)
Surface States

The surface charge is believed to reside in surface states. The states which are associated with the oxide layer are called slow states and the states which are associated with the interface between the oxide and the semiconductor are called fast states.

The oxide layer states are called slow states because their communication with the free carriers is very limited, and the time constant to achieve equilibrium with the interior is slowly established. It appears that the great majority of these states lie outside the oxide layer and their number and energy levels are controlled by ambient atmosphere. Work by Lasser et al. (7, p. 197) has shown that time constants of the slow states increase as the thickness of oxide increases. He also found that the presence of water vapor decreases the time constant and postulated that water vapor forms states on the outer oxide layer, thus increasing the state density. Time constants for the slow states are from milliseconds to minutes and with artificial layers may extend to hours. The density of slow states in germanium has been found in the order of \(10^{13}\) per cm\(^2\) to \(10^{15}\) per cm\(^2\).

Theoretical studies have indicated that there is a likelihood of the existence of fast states in the interface of oxide and crystal surface.
These states are characterized by large capture cross-sections for recombination.

The existence of these states may be due to the misfits of the oxide layer and the semiconductor material. This type of surface states has density of $10^{11}$ per cm$^2$ in germanium. Time constants for the fast states are in the range of microseconds.

**Space-Charge Region**

There exists at semiconductor surfaces, a space-charge double layer. This may originate because of the presence of surface charge of one sign. This surface charge must be compensated by the charge within the bulk material. Because of the much lower bulk charge density, the electron or hole distribution must be spread over a relatively wide region called the space charge region.

There are three distinct regions that must be considered in the space-charge region:

1. Depletion layer - the depletion layer is a region where there are ionized impurities but very few free carriers. This region usually extends about $10^{-4}$ cm into the bulk material.

2. Inversion layer (Figure 2) - this occurs when the greatest contribution to the space-charge comes from carriers of the opposite kind to those predominating in the bulk material. Thus, one would have a P-type region in an N-type semiconductor or vice versa.
Figure 2. Surface Barriers on Semiconductors

(a) Inversion Layer on N-Type Material
(b) Accumulation Layer on N-Type Material
(c) Inversion Layer on P-Type Material
(d) Accumulation Layer on P-Type Material
This layer is concentrated very close to the surface and its thickness is very small compared with the depletion layer. Therefore, the potential drop across this region can be considered negligible. The inversion layer and depletion layer may exist simultaneously as part of the total space-charge region. Actually, an inversion layer is impossible without a depletion layer existing immediately below it.

3. Accumulation layer (Figure 2) - when the surface charge has the opposite sign as the bulk material, there is an increase in the concentration of majority carriers and an accumulation layer is formed. In this case as in the inversion layer case, the charge is concentrated quite close to the surface. However, for an accumulation layer, the conductivity at the surface is the same as that of the bulk material while the surface conductivity of an inversion layer is opposite to that of the bulk material.

These surface layers satisfy Poisson's equation of neutrality. To neutralize any charge in the surface states, the energy bands must bend at the surface so that carrier concentrations are changed to give the required space-charge.
EFFECT OF SURFACE RECOMBINATION ON TRANSISTOR PARAMETERS

In the usual junction type transistors, the current amplification factor is largely controlled by the properties of surface around the emitter; and the reverse current at the collector may be greatly influenced by the surface nearby. The breakdown voltage, too, depends on the surface barriers height near the collector.

Current Gain $a$

Various factors affect the external current gain ($a$) of a transistor. The current gain depends on the emitting efficiency of the injected minority carriers ($\gamma$), the fraction of minority carriers surviving recombination in transit across the base ($\beta$), and the collector multiplication (M) may occur in the collector process.

Analytically,

$$a = \gamma \beta M$$

The emitter of a transistor is usually more heavily doped than the base. The emitting efficiency depends on the efficiency of the minority carriers flowing into the base region. Therefore, a long lifetime or small recombination is desired. However, a heavily doped material usually has a short minority carrier lifetime due to recombination effects of the impurities. Optimum design involves a
compromise between the two parameters.

\( \beta \) depends on the ratio of minority carriers arriving at the collector junction to that emitting from the emitter. A fraction of the minority carriers may recombine at the base region. Therefore, the base region should be a region of few recombination centers.

The collector multiplication (M) is a process mostly due to the effect of collisions of minority carriers which enter the high field of the base and collector junction. The minority carriers may dissipate energy by making collisions with the crystal lattice, or they may accumulate enough energy over an unusually long mean free path or over a succession of elastic collisions with the atoms of the lattice to create new electron-hole pairs by impact ionization.

**Voltage Breakdown**

The breakdown voltage depends on the surface barriers height near the collector. The breakdown voltage is due to the collisions of electrons with the atoms of the lattice in the presence of the high field existing in the junction. A small barrier height means a high voltage gradient in the junction and thus capable of accelerating the electrons. The width of the barrier depends on the impurity or the doping level of the semiconductor. In order to neutralize the surface charge, a material with a higher concentration of impurities will have a smaller space-charge region. This is due to the fact that there are
more impurity atoms per unit volume available to neutralize the surface charge. In order to have a higher breakdown voltage, a low voltage gradient in the junction is desirable. This is achieved by selecting material with a low concentration of impurities or few recombination centers.

Reverse Current

Reverse current is usually generated by thermally agitated electrons and holes within a diffusion length of the junction. Electrons and holes recombine at random fashion. Surfaces which will effect a small recombination in the material have less probability to produce reverse current at the collector junction because of the unavailability of electrons and holes to recombine. Therefore, the surface condition at either side of the junction plays an important role.
SURFACE RECOMBINATION OF SEMICONDUCTORS

When electron-hole pairs are generated in semiconductors so that nonequilibrium densities are present, they will recombine, resulting in a mutual annihilation, and approach the equilibrium distribution. The rate in which the carriers recombine to achieve equilibrium is of great interest as well as the mechanisms involved. The mobile carriers may recombine through recombination centers at discrete energy levels or simply be trapped at the surface without recombining. These phenomena usually result from the interaction of these mobile carriers with crystal imperfections and surface conditions. Crystal and surface imperfections may arise from structural or chemical reasons.

Mechanisms of Surface Recombination

The recombination of electrons and holes at a surface may be due to certain recombination centers or traps at a certain energy level in the forbidden gap as illustrated in Figures 3a and 3b.

The recombination centers, pictured in Figure 3a, are at a discrete energy level in the forbidden gap. These centers are considered to exist in either of the two electronic states. A center containing an electron must be free to lose that electron by capturing a hole. The hole once captured creates the second state of the
center. A recombination center is accessible to both the conduction band and the valence band. During recombination, an electron may be captured by the center from the conduction band. If this electron is captured by a hole from the valence band, resulting in a mutual annihilation, a recombination has just occurred. A recombination center may be described as a localized electronic level in the forbidden gap which has a high probability of exchanging carriers with both the valence and conduction bands.

There are electron or hole traps (Figure 3b), in semiconductors which accept only one type of carrier and do not contribute to the recombination process. For example, an electron trap will capture an electron from the conduction band, hold it in the trap for an interval, and then release the electron back to the conduction band.
Since the electron trap will not capture holes, there is no possibility of recombination at the trapping level. These trapping centers, unlike the recombination centers, have access to only one of the energy bands. It is possible to have electron traps in P-type semiconductors and hole traps in N-type semiconductors. In addition, there may be several trapping levels with different energies in a given semiconductor sample, and each level has traps with different relaxation times. Haynes and Hornbeck (5, p. 311) have shown that there are at least four different trapping levels in silicon.

Origins of Recombination Centers

There are various factors that affect the mechanism of surface recombinations. As mentioned before, surface recombination in the fast states is mostly due to the misfits between the oxide layer and the semiconductor crystal layer. The misfits between these two layers may be due to the introduction of foreign atoms or impurities at the surface. All these factors may contribute to the formation of recombination centers in semiconductors.

Kurtz, Kulin and Averbach (6, p. 1287) have shown that the dislocation density increases rapidly with crystal growth rate. They explained that high growth rates lead to an increasing of crystallization accidents, and the movement of the solid-liquid interface may be so rapid that all of the atoms do not have time to solidify in the
correct lattice sites. The high temperature gradients and cooling rates associated with the solid-liquid interface may cause severe lattice strains and may give rise to dislocations. They have presented evidence that the growth rate of the crystal may change the recombination efficiency as much as a factor of 10. They explained that this is due to the tendency of impurities to segregate on dislocations.

Lineage boundaries were shown by Vogel, Read and Lovell (14, p. 1791) to be regions of rapid recombination. Dislocations near the edge of the crystal act like rows of closely spaced acceptor centers. The existence of these edge dislocations is a possible source for surface recombinations. Plastically deformed semiconductors were also found by Wertheim and Pearson (16, p. 694) to be the origins of recombination centers. They found out that the surface lifetimes of crystals are inversely proportional to the dislocation densities. Other evidence also shows that radiation damage also causes the formation of recombination centers. The surface recombination rate is directly proportional to the length of time that the samples are bombarded in a high energy Van de Graaf generator (8, p. 1861).
DEPENDENCE OF SURFACE RECOMBINATION UPON CARRIER CONCENTRATION

The net rate of capture of electrons by the recombination centers as shown in Figure 3a is equal to the rate of capture of electrons from the conduction band minus the rate of emission back to the conduction band. It is shown by Shockley (12, p. 835) as

\[ U_{CN} = C_f \frac{n_{pt} n}{n_{t-1}} - C_f \frac{n_{n}}{n_{t-1}} \]  (1)

Similarly, for the net rate of capture of holes

\[ U_{CP} = C_f \frac{p_{pt} p}{p_{t-1}} - C_f \frac{p_{p}}{p_{t-1}} \]  (2)

where

- \( U_{CN} \) = net ratio of capture of electrons
- \( U_{CP} \) = net rate of capture of holes
- \( C_n \) = probability per unit time that an electron will be captured from the conduction band
- \( C_p \) = probability per unit time that a hole will be captured from the valence band
- \( f_t \) = fraction of center occupied by electrons
- \( f_{pt} \) = 1 - \( f_t \) = fraction of center occupied by holes
- \( n \) = \( N_c \exp\left(-\frac{E_c - E_F}{KT}\right) \), density of electrons in the conduction band
- \( n_{l} \) = \( N_c \exp\left(-\frac{E_c - E_t}{KT}\right) \), density of electrons in the conduction band for the case when the Fermi level is at \( E_t \)
\( p = \) density of holes in the valence band
\( p_1 = \) density of holes in the valence band for the case when the Fermi level is at \( E_t \).
\( n_o = \) electron density at thermal equilibrium
\( p_o = \) hole density at thermal equilibrium

Suppose that hole-electron pairs are being generated at a constant rate by light, or by carrier injection, the net rate of capture of electrons by the recombination centers must be equal to that of holes under steady conditions. Therefore

\[
C_n (1-f_t) n - C_f t n_1 = C_f t p - C_p (1-f_t) p_1
\]

(3)

Solving for \( f_t \), the net rate of recombination, which is equal to the net rate of capture, is obtained as

\[
R. = U = \frac{(p n - p_1 n_1) C_n C_p}{[C_n (n+n_1) + C_p (p + p_1)]}
\]

(4)

If we define that the lifetime of the minority carriers as

\[
\tau = \frac{\Delta n}{R}
\]

(5)

Substituting the rate of recombination into Eq. (5) results

\[
\tau = \frac{T_{n_o} (p_o + n_o + \Delta n)}{(p_o + n_o + \Delta n)} + \frac{T_{p_o} (p_o + p_1 + \Delta n)}{(p_o + n_o + \Delta n)}
\]

(6)
where

\[ \Delta n = \text{deviation electron density from its thermal equilibrium value} \]

\[ n = n_0 + \Delta n \]

\[ \tau_{po} = \frac{1}{C_p}, \text{ lifetime for holes injected into highly P-type specimen} \]

\[ \tau_{no} = \frac{1}{C_n}, \text{ lifetime for electrons into highly P-type specimen} \]

For a small disturbance,

\[ \tau = \frac{\tau_{po}(n_0 + n_{1})}{(p_0 + n_{1})} + \frac{\tau_{no}(p_0 + p_{1})}{(p_0 + n_0)} \] (7)

From Eq. (7), it can be seen that minority carrier lifetime depends on the carrier concentration of impurities. For low resistivity N-type semiconductor where \( n_0 \gg n_{1} \), then \( \tau \) from Eq. (7) will be equal to \( \tau_{po} \). However, for a high resistivity N-type material, \( n_{1} \) is comparable to \( n_0 \), the lifetime of minority carrier will be as

\[ \tau = \tau_{po} \frac{n_1}{n_0} = \tau_{po} \exp \left[ + \left( E_t - E_F / KT \right) \right] \] (8)

As long as \( n_0 \gg n_{1} \), the Fermi level is above the recombination centers; all the centers are filled with electrons and are available to capture holes. However, as the Fermi level moves towards \( E_t \), and the value of \( n_0 \) approaches \( n_{1} \), more and more of the centers do not contain electrons and are not able to capture holes.
Therefore, the efficiency of surface recombination decreases as the resistivity increases, because the number of electrons available to capture holes is decreasing.
PEM METHOD OF MEASURING SURFACE RECOMBINATION

If a slab of semiconductor, illuminated on one of its faces, is placed in a magnetic field parallel to the illuminated surface, a voltage is developed in the semiconductor in a direction perpendicular to the magnetic field and normal to the illuminated surface. This photoelectromagnetic voltage, which is proportional to the magnetic induction, may be considered as a special case of the Hall effect produced by diffusion current. It provides a convenient way of measuring the surface recombination velocity of semiconductors.

![Diagram of PEM method](image)

Figure 4. PEM Method of Measuring Surface Recombination Velocity
Experimental Method

The principle of the method is shown in Figure 4 which represents a side view of a slab of silicon. The intense light shining on the front surface creates a high concentration of electron and holes at that surface. If the surface recombination at the illuminated surface is not too large, most of the electrons and holes will diffuse towards the dark side. In the magnetic field, the electrons and holes tend to be deflected in the opposite directions and this sets up a difference of potential which is the quantity measured. Recombination in the interior can be neglected provided the silicon has a high volume lifetime.

For a silicon of thickness less than a diffusion length and under strong illumination, the surface recombination can be conveniently related to the photoelectromagnetic voltage as follows (11, p. 307),

\[ E_x = -BS \] (9)

or

\[ \frac{V_x}{\ell} = -BS \] (10)

\( V_x \) is the voltage to be determined, \( S \) in cm/sec is the surface recombination velocity, and \( B \) is the magnetic field. In the present work, a permanent magnet with magnetic field strength of 5000 gauss is used. The light source is room illumination light with an
intensity of 22 ft-candles.

Experimental Techniques

The silicon specimens used were 2.0 x 0.5 and 0.05 cm. in dimensions. The thickness is less than a diffusion length, since the silicon used has a bulk lifetime of approximately 500 microseconds, and the diffusion constant for silicon is 31 cm.$^2$ per sec. The silicon sample was lapped with carborundum and rinsed in distilled water before contacts were attached.

Ohmic contacts can be made successfully to silicon by alloying gold doped with antimony for an N-type sample or gold doped with gallium for a P-type sample to the silicon. The eutectic temperature for gold and silicon is at 370°C. The alloying process was carried out by means of a strip-heater in the presence of forming gas atmosphere. After the gold is alloyed to the silicon sample, the two copper wire contacts can be easily soldered to the gold.

In order to compare the effect of various etches on the surface recombination velocity of silicon, an experiment was performed in which only the front surface or the illuminated side is etched while the back surface is lapped. That is, if the front surface is a good surface, little recombination will occur; most of the electrons and holes will diffuse across to the back side resulting in a large photoelectromagnetic voltage. Whereas a poor surface will give a
small photoelectromagnetic voltage at the dark side. The back surfaces of all the silicon samples were lapped with carborundum while the front surfaces were subjected to various etching treatments. In order to avoid etching at the back surface, masking was employed. Polystyrene was found satisfactory. However, a sealing compound, Apiezon W, when diluted in trichloroethylene was satisfactory and easier to apply.

The determination of actual values of surface recombination velocity must depend on a knowledge of the surface recombination mechanism. The amount of impurities in the material may contribute certain donor or accepter types of surface recombination centers. Silicon samples with various resistivities were lapped on the back surfaces while the front surfaces were treated with CP-4; and the photoelectromagnetic voltage which is proportional to the surface recombination velocity was determined from each sample.

**Experimental Results**

N-type silicon with a resistivity of 480 ohm-cm was used. The contacts were kept constant at a distance of 1.3 cm. apart, and a magnet with a field strength of 5000 gauss was used. From Eq. 1, it can be seen that surface recombination velocity is directly proportional to the photoelectromagnetic voltage $V_x$ at the back surface. The magnitude of this voltage on the back side depends on how much
Table I. * PEM Measurements for Various Etches Applied to the Illuminated Surface

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<td></td>
<td>5.0</td>
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</table>

* Please refer to Appendix for the compositions of etches.
recombination has taken place on the front surface, thus allowing a comparison among the various treatments. CP-4 etch gives a large photoelectromagnetic voltage compared to the others (Figure 5). In other words, CP-4 provides a good surface where little surface recombination occurs. A Superoxol treatment gives a silicon surface with a very large surface recombination velocity.

Various resistivities of silicon specimens were etched for 1 minute in CP-4 on the illuminated side. The data shown in Table II indicate that the higher the resistivity, the higher the photoelectromagnetic voltage obtained at the dark side. This may be explained in terms of the conduction process in the semiconductor. A high resistivity material represents a material with few impurities and a low number of recombination centers. If there is less chance for the minority carriers generated at the surface to recombine, most of the minority carriers will then diffuse to the back surface resulting in a large photoelectromagnetic voltage.

It was found that the surface recombination velocity of the treated silicon varied slightly from batch to batch of supposedly identical etch. This variation may be due to the fact that the etching action is usually initiated at small surface imperfections such as pits and scratches, and thus the microscopic condition of the surface, which is impossible to reproduce exactly for each trial, plays an important role in the etching process. Small local
Figure 5. PEM Voltages for Various Etches as a Function of Etching Time
Table II. PEM Measurements of Silicon Etched 1 Minute in CP-4 on the Illuminated Surface

<table>
<thead>
<tr>
<th>Resistivity (OHM-CM)</th>
<th>Vx (MV)</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>0.2</td>
</tr>
<tr>
<td>53</td>
<td>0.8</td>
</tr>
<tr>
<td>128</td>
<td>1.5</td>
</tr>
<tr>
<td>240</td>
<td>3.0</td>
</tr>
<tr>
<td>480</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Variations in bulk lifetime from sample to sample may cause a variation in experimental values. All etching solutions were allowed to stand 1/2 hour before use.
LIFETIME OF MINORITY CARRIERS

Experimental Method

Lifetime of minority carriers are measured by the change in conductance of a semiconductor sample due to excess injected minority carriers; the minority carriers are injected optically. The excess conductance is proportional to the number of excess minority carriers and the resulting change in voltage across the sample will be proportional to the excess conductance. The resulting change of voltage across the crystal is amplified and displayed on an oscilloscope.

If an excess of minority carriers is produced on the surface of silicon, these minority carriers will decay with time as

$$\frac{dn_1}{dt} = -\frac{n_1}{\tau}$$

(11)

where \(\tau\) is the lifetime of the excess free minority carriers, and \(-dn_1/dt\) is the rate at which the excess minority carriers are annihilated by recombination with majority carriers.

The time constant for the decay of photoconductivity can be determined by illuminating the silicon with a pulsed light source. A constant current is supplied through the silicon sample, and the resulting change in voltage \(\Delta V(t)\) is amplified and displayed on an oscilloscope.
If the crystal is sufficiently uniform, the current flow will be paralleled to the crystal axis. If the added minority carriers density is small compared with the majority carrier density, the lines of current flow will not be affected appreciably by the injection. The change in voltage can be computed by integration along the crystal axis (x-axis).

\[
\Delta V(t) = \int_{\text{crystal}} \frac{<\Delta \sigma (x, t)>}{<\sigma (x)>} E(x) \, dx
\]

where \( E \) is the electric field and \(<\Delta \sigma (x, t)>\) and \(<\sigma (x)>\) are the average value of change in conductivity and conductivity respectively.

Instrumentation

A block diagram of the apparatus used to observe the photoconductive decay is shown in Figure 6. The pulsed light is focused on the silicon crystal, which carries a constant current. The resulting change in voltage is amplified and displayed on an oscilloscope. Since one wishes the photoconductive decay curve to be a characteristic of the crystal itself, it must also be able to turn off the light in a time short compared to the carrier lifetime. For this work, a xenon flash tube model FX-6A manufactured by EG and G was used. The FX-6A is triggered by a low current, high voltage,
Figure 6. Block Diagram for Measuring Lifetime of Minority Carriers by Photoconductive Decay Method
positive pulse capacitively coupled to the trigger probes of the tube. The triggering voltage is 2.5 KV. The turn off time of the pulse was measured by RCA type 917 photo-detector tube to be 0.8 microsecond. The pulse repetition rate is 60 pulses per second. To avoid electrical and acoustic noise, the light source is encased in a light-tight black box with aluminum foil wrapped around it for shielding. The circuit diagram for the pulsed light source is shown in Figure 7.

The transient response of the required system depends on the minimum and maximum lifetimes one wishes to measure. The rise time of the presentation system must be short compared to the minimum lifetimes to be measured. Therefore it is advisable to use silicon crystals with long volume lifetime. It is also important that the noise figure of the system be low.

A Tektronix type 516 oscilloscope equipped with a type 121 preamplifier was used. The bandwidth of this unit is from 3 cycles to 17 megacycles and has a sensitivity of 5 mv/cm. The resistor in series with the silicon crystal should be at least 10 times the resistance across the crystal in order to maintain a constant current. The current was supplied by a battery.

Experimental Techniques

A P-type silicon crystal with a resistivity of 2000 ohm-cm and
Figure 7. Circuit Diagram for the Pulsed Light Source
a volume lifetime of over 1 millisecond was used. The silicon specimens used were 1.0 x 0.5 x 0.05 cm in dimensions. The samples were lapped with #600 grit silicon-carbide powder and then rinsed in distilled water. Ohmic contacts were put on the P-type sample by first alloying the contact area with gold doped with gallium. Copper wires then were soldered to the contacts.

Light striking a junction in the crystal will result in a photovoltage. This photovoltage will be detected by the presentation system and may be similar in amplitude and time dependence to the photoconductive signal. This photovoltage can be eliminated by observing that illuminating the crystal does not give rise to a signal if the constant current source is set at zero.

Trapping of the minority carriers may give rise to an inaccurate measure of the minority lifetimes. Since the mechanism of surface recombinations through recombination centers is the only thing to be investigated, the effects of trapping can be eliminated by exposing the crystal to a moderate amount of ambient light which has the effect of filling the traps.

If the lifetime measurement is to be accurate, the density of added carriers must be small compared to the majority carrier density in the region of the crystal where the lifetime is measured. Also the field must be small so that the added carriers will not drift into regions of different electric field, conductivity, or lifetime
during the measurement. To check experimentally that the electric field being used is not too high, it is generally sufficient to reverse the current flow in the crystal and compare the measure lifetime.

**Experimental Results**

The experimental results are listed in Tables III and IV. The listed minority carrier lifetimes are the averages over 7 samples for each treatment. CP-4 gives the highest minority carriers lifetime in silicon; a Superoxol etch results in a minority carrier lifetime even lower than a lapped surface. Sodium dichromate solution and hydrofluoric acid have the effect of lowering the minority carrier lifetime in P-type silicon.

A series of atmospheres of dry oxygen, nitrogen, argon and water vapor were exposed to the P-type silicon specimens after various treatments: 1. etched in CP-8, 2. etched in CP-8 and soaked in hydrofluoric acid, 3. etched in CP-8 and soaked in sodium dichromate solution; no obvious change in minority carrier lifetime was observed due to the changes of atmosphere.
Table III. Lifetime of Minority Carriers in P-Type Silicon after 1 Minute Etch

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Minority Carrier Lifetime (Microseconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lapped Surface</td>
<td>10.0</td>
</tr>
<tr>
<td>CP-4 Etch</td>
<td>24.0</td>
</tr>
<tr>
<td>CP-8 Etch</td>
<td>16.0</td>
</tr>
<tr>
<td>WAg Etch</td>
<td>11.0</td>
</tr>
<tr>
<td>CU Etch</td>
<td>10.0</td>
</tr>
<tr>
<td>Superoxol Etch</td>
<td>8.0</td>
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</tbody>
</table>

Table IV. Lifetime of Minority Carriers in P-Type Silicon after Etched in CP-8, and Soaked in Various Solutions for 5 Minutes

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Minority Carrier Lifetime (Microseconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF Soak</td>
<td>7.0</td>
</tr>
<tr>
<td>Sodium Dichromate</td>
<td>5.0</td>
</tr>
<tr>
<td>Boiling Water</td>
<td>16.0</td>
</tr>
<tr>
<td>HNO₃ Soak</td>
<td>16.0</td>
</tr>
<tr>
<td>KOH Soak</td>
<td>16.0</td>
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</table>
CONCLUSIONS

The properties of semiconductors are sometimes governed by the surface properties near by rather than by the bulk property of the material. An understanding of the surface properties of semiconductors usually lead to an improvement of certain electrical parameters. In particular, the effect of surface recombination on the current gain, reverse current, and the voltage breakdown often limits the optimum performance of a transistor.

The photoelectromagnetic effect provides a convenient way of comparing surface recombination velocity in semiconductors. The time for the minority carriers to survive recombination can also be observed by the decay of photoconductivity. A large surface recombination in semiconductors usually results in a short minority carrier lifetime. For example, CP-4 etch on silicon surface results in a long minority carrier lifetime but very little surface recombination whereas Superoxol etch produces large surface recombination on silicon but a comparatively short minority carrier lifetime. The photoelectromagnetic measurements comply very well with the results of photoconductive decay; the minority carrier lifetime is inversely proportional to the surface recombination velocity.

Sodium dichromate solution has the pronounced effect of increasing surface recombination in silicon. Ambient atmospheres
seem to have no obvious influence on the surface recombination property of silicon.
BIBLIOGRAPHY


APPENDIX

COMPOSITIONS OF VARIOUS ETCHES

<table>
<thead>
<tr>
<th>Etches</th>
<th>Compositions</th>
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<tbody>
<tr>
<td>CP-4</td>
<td>120 c.c. acetic acid</td>
</tr>
<tr>
<td></td>
<td>120 c.c. hydrofluoric acid</td>
</tr>
<tr>
<td></td>
<td>200 c.c. nitric acid</td>
</tr>
<tr>
<td></td>
<td>44 drops bromine</td>
</tr>
<tr>
<td>CP-8</td>
<td>120 c.c. acetic acid</td>
</tr>
<tr>
<td></td>
<td>120 c.c. hydrofluoric acid</td>
</tr>
<tr>
<td></td>
<td>200 c.c. nitric acid</td>
</tr>
<tr>
<td>Superoxol</td>
<td>10 c.c. concentrated hydrogen peroxide</td>
</tr>
<tr>
<td></td>
<td>10 c.c. concentrated hydrofluoric acid</td>
</tr>
<tr>
<td></td>
<td>40 c.c. distilled water</td>
</tr>
<tr>
<td>WAg</td>
<td>4 c.c. concentrated hydrofluoric acid</td>
</tr>
<tr>
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<td>2 c.c. nitric acid</td>
</tr>
<tr>
<td></td>
<td>4 c.c. distilled water</td>
</tr>
<tr>
<td></td>
<td>200 mg. silver nitrate</td>
</tr>
<tr>
<td>CU</td>
<td>4 c.c. concentrated hydrofluoric acid</td>
</tr>
<tr>
<td></td>
<td>2 c.c. nitric acid</td>
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<tr>
<td></td>
<td>4 c.c. distilled water</td>
</tr>
<tr>
<td></td>
<td>200 mg. cupric nitrate</td>
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