Application of Surface Photovoltage in Online Monitoring of IC Oxide Layer and Oxidation Furnace Tube

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Abstract: Surface photovoltage (SPV) is an online monitoring technology with high sensitivity and non-destructive characteristics. It can accurately measure the minority carrier diffusion length and lifetime of semiconductor wafers, heavy metal contamination concentration and other parameters. It plays an important role in the online monitoring of IC oxide layer and oxidation furnace tube, and is also an important detection method to ensure the quality of IC production. As the integrated circuit continues to evolve, the requirements for online contamination monitoring technology are constantly increasing. The most common impurities in the IC manufacturing process are heavy metals, which have a severe impact on the quality of the oxide layer and reduce the reliability and yield of the associated device. By applying SPV, relevant samples can be quickly tested and monitored online, which is widely used in the research and production of integrated circuits. In this paper, the surface photovoltage is analyzed and its application in the online monitoring of IC oxide layer and oxidation furnace tube is discussed.

1. Introduction:

With the rapid development of science and technology in China, the research of integrated circuits has become more and more intensive, gradually entering the sub-micron and deep sub-micron size and special circuit fields, continuously adopting MOS thin gate oxidation process, and also increasing the requirements of contaminated online monitoring technology. When the thickness of the oxide layer is 20 nm, the generally allowed metal contamination concentration can reach. When the thickness of the oxide layer is 10 nm, the contamination concentration of the metal has a sensitive effect on the performance of the oxide layer, but the concentration cannot exceed $8 \times 10^{10} / cm^3$. As a highly sensitive and non-destructive online monitoring technology, surface photovoltage plays an important role in the production of IC. Using the surface photovoltage technology to measure the IC silicon wafer, the parameters such as the minority carrier lifetime, the concentration of heavy metal impurities, and the surface recombination velocity of the IC wafer can be obtained. For the lifetime of minority carriers in silicon wafers, there is a direct relationship between them and their lattice structure, and these two important physical parameters can reflect the quality of the silicon wafer. By using SPV to measure the silicon wafer, the reliability and yield of the product can be further improved, and it plays an important role in the research and production of integrated circuits.

2. Surface Photovoltage (SPV) Analysis

2.1 Basic principles

When light strikes the surface of the silicon wafer, if the silicon surface accepts photon energy that is significantly above the forbidden band, it will inevitably result in hole-electrons near the surface of the sample. The surface of the silicon surface is affected by certain hole-electron diffusion, and the electric field separation causes photovoltage on the silicon surface. After the silicon surface photovoltage reaction test, the corresponding L (minority diffusion length) can be obtained. Use $\tau$ for life and $N_e$ for heavy metal contamination. There must be a correlation
between L, \( \tau \), and \( N_e \). The formula is as follows: 

\[
L = \sqrt{\frac{kT}{q}} \mu \tau
\]

and . ., and corresponding calculation can be obtained . . and . . For regions near the surface of the silicon, if there are more unbalanced carriers, then a larger surface photovoltage will also be produced. When using SPV measurement on silicon wafers, attention should be paid to the surface barrier of the silicon wafer, which is mostly available for the IC wafers currently used for production. Therefore, for most types of silicon wafers, SPV technology can be used when measuring the minority diffusion length in the case where the resistivity is greater than 0.1\( \Omega \). For P-type Si substrates, the corresponding \( Fe-B \) bond can be formed during the test, so SPV technology can be used for rapid measurement of heavy metal contamination. When using SPV technology for measurement, some silicon surface is exposed to oxygen and nitrogen, and even some of the silicon surface and photoresist are highly susceptible to metallization. Therefore, it should be ensured that the silicon surface and the graphic composition are not 100% protected from light, so that the accuracy of measuring the final data is high.

2.2 Surface photovoltage measurement technology

SPV measurement techniques are mostly used when measuring the lifetime of unbalanced minority carriers. According to the relevant excitation mode of the minority in the semiconductor, when measuring the lifetime of the minority carrier, the measurement methods that can be used are transient and steady state methods. For SPV measurement technology, it is a steady-state method that is more commonly used. Under the condition of stable illumination, the stable distribution of unbalanced minority carrier can be maintained, and the life of the minority carrier is accurately and quickly calculated.

2.2.1 Measuring \( Fe \) contamination concentration using SPC

The metal contamination in the silicon wafer will cause some damage to the performance of the oxide layer, which has a serious impact on the development of the integrated circuit process. Heavy metal impurities may be present in the original silicon wafer and may also occur in other parts of the IC process. In general, heavy metals in silicon wafers exhibit iconicity, and the state in their silicon lattice determines their effect on the electrical properties of silicon devices. The dissolution of heavy metals in silicon results in a reduction in minority life. If a precipitation reaction occurs in such a heavy metal, a silicon surface defect occurs, which in turn affects the overall reliability of the silicon device.

In the process of semiconductor manufacturing, the commonly used material is stainless steel, so the heavy metal impurities such as \( Fe \) are mixed. At normal temperature, \( Fe \) will exist in P-type silicon in the form of \( Fe-B \). A simple heat treatment of the silicon wafer causes the \( Fe-B \) bond to break, and \( Fe \) will exist in the corresponding gap position, thereby forming an efficient recombination center in the silicon wafer.

Before and after the heat treatment of the silicon wafer, it is necessary to carefully observe the change of the length of the minority diffusion, and the concentration of \( Fe \) can be effectively measured. If the heat treatment is replaced by light, the \( Fe-B \) bond can be separated, and the concentration of \( Fe \) is:

\[
N_{Fe}(cm^{-3}) = C(L_1^2 - L_0^2)
\]

(1)

Where the excitation type of the minority is determined by the calibration constant C. Under the heat treatment conditions of 200 °C, the calibration constant is most typical of \( C = 1.5 \times 10^{16} \), which takes into account the partial deactivation properties of \( Fe \). For the silicon wafer before and after the heat treatment, the minority carrier diffusion length can be expressed by \( L_0 \), \( L_1 \), and can be measured using SPV according to the corresponding principle. By using a corresponding optical filter, the corresponding luminous flux is stabilized at H, and any wavelength has \( H_{eff} = H(1 - R) \)
after the corresponding emission, where R represents the reflectivity. For incident light of different wavelength $\lambda$, the photovoltage signal of the silicon surface under irradiation is $\Delta V_0$, $T$ is the corresponding absorption coefficient of $\lambda$, and there is $Z = T^{-1}$, so the photovoltage of the small signal surface can be expressed as:

$$\Delta V = ConstH_{\text{eff}} f(z)$$  \hspace{1cm} (2)$$

where $f$ is a function of the transmission depth $z$ and can be expressed as

$$f(z) = \frac{1}{1 - z^2/L^2} \left(1 - \frac{Bz}{L}\right)$$  \hspace{1cm} (3)$$

Where B is related to the diffusion velocity $v$ and the back composite velocity $S_b$. The diffusion speed $v = D/L$, when distinguishing the size of $S_b$, the concave and convex of the correlation graph of $\Delta V$ and $z$ can be utilized.

The appropriate SPV signal to be alive during the relevant experiments can be performed by adjusting the incident light flux. After determining the relationship between the surface photovoltage and the diffusion length, a corresponding SPV signal can be obtained by performing a corresponding measurement with a luminous flux value of 2.0, and then the diffusion length of the minority carrier is determined. When SPV is used, the calibration constant of the optical activation parameter is the same as that of the thermal activation parameter, so that the corresponding minority carrier diffusion length can be calculated under different methods, thereby obtaining an accurate $Fe$ concentration. In this process, the measurement of the minority carrier diffusion length $L_0$ before activation requires a pair of $Fe$ ions and B ions.

### 2.2.1 Ways to measure the diffusion length of a minority carrier

When using SPV measurement technology, when measuring the minority carrier diffusion length of different sample conditions, there are generally two similar cases. When the sample has a minority carrier diffusion length $L < 75\% T_{Si}$, the SPV corresponding measurement method is “standard mode”. When the minority carrier diffusion length of the sample is $L > T_{Si}$, the measurement method corresponding to the SPV is “enhanced mode”. Furthermore, the relationship between the surface photovoltage $\Delta V$ and the diffusion length L can be correspondingly simplified.

(1) “Standard mode” corresponding to SPV

When the diffusion length of the sample is $L < 75\% T_{Si}$, it is a case of a short diffusion length. If $T / L \geq 2$, $\sinh(T / L) \approx \cosh(T / L)$, then the calculation according to the relevant formula can obtain $B \approx 1$, and then the formula (2)~(3) can be simplify to as follow:

$$\frac{1}{\Delta V} = H_{\text{eff}} Cond (1 + z / L)$$  \hspace{1cm} (4)$$

According to the formula, it can be found that when the surface photovoltage signal is extremely large, $\frac{1}{\Delta V} = 0$, at which time the values of the minority carrier diffusion length and the transmission depth are equal. If the corresponding surface light voltage values and their corresponding $\frac{1}{\Delta V}$ and $z$ are plotted, the corresponding linear relationship can be obtained, as shown in Fig. 1.

(2) “Enhanced mode” corresponding to SPV

When the diffusion length of the sample is $L > T_{Si}$, this indicates that the diffusion length of the silicon wafer is approximately equal to or more than the thickness of the silicon wafer. In this case,
the value of $B$ cannot be taken 1. When $(Z/L)^2 \leq 1$, (2)–(3) can be simplified to the follow:

$$\Delta V = H_{eff} \, \text{Const} \left(1 - Bz/L\right) \quad (5)$$

For silicon wafers with oxidized surface, they have a higher back recombination velocity. In the case where the diffusion length is long enough, the ratio of diffusion speed to $S_b$ is negligible, at this time $B = \frac{\cosh(T/L)}{\sinh(T/L)}$.

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Figure 1. “Standard mode” corresponding to SPV

3. Application of Surface Photovoltage Technology in Online Monitoring of IC Oxide Layer and Oxidation Furnace Tube

3.1 Using SPV to test the diffusion length of silicon and the concentration of Fe ions

In Fig. 2, nine sets of measurement data are presented, which are 9 measurement points uniformly distributed over the $\phi 150\text{mm}$ disk area. The minority carrier diffusion length and Fe ion concentration are included in each set of data, as well as the concentration of Fe ions and other ion contamination. According to the relevant requirements, the life value of the corresponding minority carrier can be calculated by using the corresponding program. In addition to the raw data existing on the wafer, there are a total of 9 other sets of data such as maximum, minimum, mean, and root mean square difference. After careful observation of the data, a better understanding of the uniformity of the relevant measurement results can be achieved, thereby achieving the purpose of rapid detection using SPV.

Figure 2. Measurement results of 9 sets of data for a single sample

3.2 Using SPV to detect the quality of the oxide layer corresponding to different HCl flows

In the process of improving the quality of the oxide layer, the addition of $HCl$ is an important method and has been widely used in IC processes. The corresponding test was carried out using SPV measurement technology. For the oxide layer samples under different process conditions, the minority carrier diffusion length and $Fe$ ions were qualitatively observed to effectively determine the range of process conditions for $HCl$ oxidation. The thickness of the oxide layer of the relevant
sample in this experiment is 20 nm. When the oxidation was carried out, the relevant temperature was 1000 °C, and the flow rate of \( \text{O}_2 \) used in the chlorine-doping oxidation was \( 2L/min \). During the experiment, the flow rate of the \( \text{HCl} \) was \( 5ml, 10ml, 15ml, 20ml \) per minute, and the relevant test results obtained by using the SPV measurement technique were obtained. According to the analysis of the relevant test results, it can be determined that the flow ratio of \( \text{HCl} \) and oxygen is more suitable at \( \frac{1}{1000} \).

### 3.3 On-line monitoring of Fe contamination concentration in thin oxide and oxidation systems

By using SPV measurement technology, \( \text{Fe} \) contamination in thin oxide and oxidation systems can be monitored accordingly, enabling periodic online monitoring of tunnel oxide and oxidation systems on IC production lines. The relevant sample was annealed by \( \text{Ar} \) gas at a temperature of 700 °C, and when the temperature was raised to 850 °C, the corresponding \( \text{HCl} \) was added for oxidation. In this process, the flow ratio of \( \text{HCl} \) to oxygen is \( \frac{1}{1000} \), followed by high temperature annealing under the action of \( \text{N}_2 \). For \( \text{Fe} \) contamination in thin oxides and oxidation systems, over \( 8E10/cm^3 \) as an alarm signal for tunnel oxidation systems. Once this signal is sent, the IC production line needs to immediately take the corresponding treatment measures to ensure the quality of the oxide layer.

### 3.4 Online monitoring of Fe contamination concentration in thick oxide layer

By applying SPV measurement technology, regular on-line monitoring of \( \text{Fe} \) contamination in thick oxide and oxidation systems is also possible. As shown in Fig. 3, according to the analysis of the corresponding online monitoring results, it can be found that when the \( \text{Fe} \) contamination exceeds \( 50E10/cm^3 \), measures should also be taken for the oxidation system alarm system to ensure the quality of the general oxidation system.

![Figure 3. SPV online monitoring of the Fe contamination concentration in thick oxidation systems](image)

### 4. Related Test Results and Discussion

#### 4.1 Detection range of SPV measurement technology

Measurement of the contamination concentration of \( \text{Fe} \) using SPV measurement techniques has proven to be a more effective method. When the SPV measurement technique is used to measure the contamination concentration of \( \text{Fe} \), the corresponding detection limit is \( 10^9 \text{cm}^{-3} \) orders of magnitude. If other composite centers are present, the sensitivity of the SPV technique to detect the contamination concentration of \( \text{Fe} \) is reduced. To measure \( \text{Fe} \) at a concentration of \( 10^9 \text{atoms/cm}^3 \), it is necessary to have a diffusion length of several hundred microns. In the presence of other recombination centers, the diffusion length will decrease and the corresponding detection limit will rise to a larger value. In addition to the use of SPV measurement technology for the detection of heavy metal contamination, the use of this technology can also measure the relevant net effect for all non-ionic composite centers. For non-metal related composite centers, dislocations and oxygen
deposition are usually included, but they do not occupy a dominant position for the occurrence of such non-metallic impurities in common situations. Therefore, the effective concentration formula of the non-ionic composite center is as follows: \[ N_R \approx 1.1 \times 10^{15} \left( \frac{P}{L_0} - 1/L_1^2 \right) \].

4.2 Problems related to SPV testing

4.2.1 Sample processing before testing

When performing SPV measurements, it can be found that when some samples have a signal \( \leq 1 \ \text{mV} \) and a correlation \( \leq 0.89 \), the occurrence of these phenomena is usually caused by the IC process. For example, the composite traps on the silicon surface and the radiation damage caused by plasma etching, and the instability of the surface of the silicon wafer after chemical treatment, will result in a decrease in the SPV signal. Further, a metal such as copper or aluminum precipitated after chemical treatment is adsorbed on the surface of the sample, but after being immersed in the HF solution for a certain period of time, it can be removed by rinsing with demonized water. The elimination of radiation damage can be carried out by rapid thermal processing, typically at 1100 °C for 4 minutes.

4.2.2 Methods for eliminating surface effects

In the process of applying SPV measurement technology, the measurement of metal substance concentration is performed by using the differential penetration depth method corresponding to different wavelengths, which can eliminate the distortion caused by long wavelength filters on near surface defects. Because the SPV cannot accurately measure the surface of the sample, when monitoring the cleaning equipment of the IC process, the tube annealing and RTP method are generally used to push the contamination into the corresponding sample body, and then the corresponding measurement is performed. However, the application of the RTP method should fully consider the exclusion of contamination from the RTP method itself.

5. Summary

In summary, the surface photovoltage technology has high sensitivity and non-destructive characteristics, and can accurately measure the parameters such as the minority sub-diffusion length and lifetime of the semiconductor wafer and the concentration of heavy metal contamination. It plays an important role in the online monitoring of IC oxide layer and oxidation furnace tube, and is also an important detection method to ensure the quality of IC production. Rapid testing and online monitoring of relevant samples can be achieved by applying SPV technology. By using SPV to measure the silicon wafer accordingly, the reliability and yield of the product can be further improved. This technology has been widely used in the research and production of integrated circuits.

References


