Application of Anodic Oxidation to Interconnect System*

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An extensive experimental work in anodic oxidation has shown that selective growth of non-porous alumina and porous alumina is possible, using photoresist and anodic barrier oxide as a respective mask. This result was carefully examined and applied to the development of new aluminum interconnections of silicon integrated circuits. In this structure which is characterized by the planar surface of alumina-covered interconnect layer, an anodic oxide film plays a key role as a protective layer against possible mechanical scratches and chemical degradation, and as a surface passivation layer of thermally grown SiO2 beneath it. Furthermore, it has been revealed in the subsequent experiment of electromigration that this new fabrication method improves a materialistic quality of evaporated aluminum. Here in this paper, a general survey on the anodizing phenomena and an attempt at interpretation based upon several qualitative facts will be presented in stead of a rigorous quantitative discussion. Some resultant data obtained from the application of this structure to MOS devices and bi-polar low noise transistor will also be shown.

1 Introduction

In the field of silicon integrated circuits, aluminum has long been considered to be the only logical choice as an interconnecting material of a single metal. It has a high electrical conductivity, adheres well to oxides, forms low resistance contact to n type and p type silicon, and is easily etched without dissolving SiO2, and above all, it is economical. Therefore, it is a common practice nowadays that aluminum, deposited to a uniform thickness, is subjected to selective etching using photoresist as a mask, to obtain necessary interconnecting lines. This etched aluminum interconnect system—simple yet useful as it is—has several drawbacks which might possibly become increasingly vulnerable as related to the high reliability of semiconductor devices: it reacts easily with almost all acids and alkalis, doesn't resist mechanical scratches on one hand, while on the other hand, it causes electromigration which gives rise to void formation and whisker growth when it carries electric current under some specific conditions. In order to compensate for the first category of shortcomings, these etched aluminum interconnect lines are often covered with an insulating material deposited by r-f sputtering or CVD method at relatively low temperatures. Concerning the serious problems caused by electromigration, which are presumed to originate partly from crystalline defects of the metal, the better result seems to be expected only by improvement of the metallic structure, on the molecular level, by some means.

In search of an ideal structure for a metal interconnect system, the research work was continued until finally anodic oxidation of aluminum made its appearance as a promising technology of application.

2 Aluminum Anodization

Anodization or anodic oxidation is a term denoting a phenomenon of a metallic surface, which occurs when the metal is given a positive potential in an appropriate electrolyte or in an oxide plasma. It has been used extensively in the capacitor industry over the past fifty years. Today it plays a basic role in microcircuitry and in thin film protection of space industry, and is the subject of renewed interest both from a practical and a theoretical point of view.

The basic principle of the phenomenon is that the transport of metal or oxygen ions through the oxide film, which must occur for the metal to grow, is aided by the electric field which is established in the film by the applied voltage. Besides some important fundamental problems involving a molecular structure of the film and an ion transport mechanism of its growth, which are still a matter of theoretical controversy even at present, much knowledge on anodization is available for practical application. Here is a summary of some generally accepted facts, with the special emphasis on aluminum anodization,
covering the scope of this paper.

2.1 Various types of oxides

Two distinct types of oxide films may be formed on aluminum by anodic oxidation, depending on the rate at which the oxide is dissolved by the electrolyte during the oxidation. Where there is little or no solvent action (oxide-nondissolving electrolyte), thin non-porous films, whose thickness is proportional to the applied voltage are formed rapidly. The growth rate of the oxide is reportedly 14 Å/V, regardless the nature of an oxide-nondissolving electrolyte. When there is appreciable solvent action (oxide-dissolving electrolyte), a relatively high steady current flow and continued growth of porous films are observed as long as the aluminum is supplied with a positive electric potential. The dissolution of the oxide in the electrolyte has been accepted as the direct cause of the pore development and the reason why anodizing does not stop in spite of the oxide films, built up on the aluminum surface. It has been shown by electron microscopy that porous films contain a hexagonal array of pores, each of which extends from the solution inwards almost to the metal surface. The base of each pore is separated from the metal by a thin non-porous layer of oxide, which constitutes an effective barrier between the metal and its environment during service. Hunter and Foule have found that the barrier thickness of the pore base formed in sulfuric acid is close to 10 Å/V.

A third type of oxide is a combination of non-porous and porous oxides. The idea was to begin anodization with a porous oxide of the desired thickness, and then to follow this by a second anodization in the oxide-nondissolving electrolyte, in the hope that the pores would be filled by the latter type of oxide. This assumption of pore-filling and conversion of a porous film into a non-porous film has been supported to be true by electron microscopy. Church and Wilson have reported that the insulating resistance and breakdown voltage are higher with the composite oxide film than with the simple non-porous one. As a variation of the composite oxide explained above, porous oxide film of any desired thickness with a barrier layer of any desired thickness at the bottom can be readily formed.

2.2 Ion transport in the oxide film

There are three possibilities of ion transport in an anodic oxide film: aluminum moves outward through the film, oxygen moves inward, or both processes take place. Depending on which of the three is in fact realized, the oxide film will be growing at the oxide-solution interface, at the metal-oxide interface, or somewhere between the two interfaces. In the case of porous type oxide, the growth of further oxide must take place somewhere between the pore bases and the metal. With aluminum, it is now generally accepted that not only are both metal and oxygen ions mobile but they are mobile to about equal extent.

2.3 Annealing of the anodic oxide

Annealing anodic oxide films results in the loss of water which is assumed to have incorporated into the oxide structure during the formation. This effect is important with such films as these prepared in sulfuric acid. With the presence of water, sulfate ions included in oxide pores may damage the film.

Regarding the effects of annealing on ionic conductivity, Vermilyea and Dignam have proposed that the structure of the oxide is altered to some degree by the annealing, which results in a drastic reduction in the number of potential carriers.

3 Selective Growth of Anodic Oxide

It is generally pointed out that a success in pattern generation of microcircuits depends much upon photoresist technology. Until recently, this technology has shown its effectiveness, almost exclusively, with the combination of the chemical etching process. The principle of this method—photo-engraving—is that an appropriate chemical agent dissolves away an unnecessary area from SiO₂ or aluminum to form diffusion windows or interconnecting paths, respectively. It has been known in this art that prolonged exposure of patterned photoresist to an etchant invariably entails degradation of its adhesion to a substrate material at side edge portions of photoresist. This effect is presumably due to an attack of anions in the etchant. In the case of anodic oxidation of aluminum, the role of photoresist as a protective means to electrochemical reaction is not so simple as of chemical etching.

In an attempt to determine the feasibility of commercially available photoresists, KPR (35 cp), KMER (35 cp) and AZ 111 as a barrier film against the growth of anodic oxide, a series of experiment was conducted. AZ 111 is a positive working photoresist, so the part that is exposed to ultra-violet light is developed off, contrary to KPR and KMER action. Each photoresist was applied, at 4000 r.p.m. by whirler coating method to the thickness of 0.4 μ, onto a 1 μ aluminum film which had been evaporated on thermally grown SiO₂. After the standard photoresist process the aluminum film was subjected to anodic oxidation of two types. An ethylene glycol solution saturated with ammonium borate and an aqueous solution of 2% sulfuric acid (by volume) were employed respectively to form non-porous and porous oxide by
constant voltage anodization. It was shown that in the first electrolyte, these photoresists acted as a good barrier up to the applied voltage of 60~80 V (This distribution of the maximum potential was presumably due to varied chemical states of the aluminum surface.). In case the anodic potential was higher, the non-porous oxide growth of semicircular shape was observed along the periphery inward from the photoresist.

In the second electrolyte, on the other hand, none of these photoresists withstood 20 V anodization even for a minute, during which aluminum could be converted into the oxide only to a depth of 1,000 Å at the most. The results were, more or less, the same with the other oxide-dissolving electrolytes such as 10% aqueous oxalic acid or 10% aqueous phosphoric acid. It was therefore concluded that photoresist does not prevent the continuous growth of porous oxide, even if a comparatively low voltage is applied for anodization.

The experimental results described above indicate that, when a total amount of charge for anodization exceeds a certain value, an edge of photoresist no longer resists the growth of anodic oxide. As the voltage, applied between the cathode and the aluminum film drops almost entirely across the oxide, (assuming resistivity of the oxide to be far greater than that of an electrolyte, which is always the case with aluminum anodization), no significant electric attraction from the anode—aluminum—acts on anions in the electrolyte. A concentration of anions near the photoresist, therefore, is much the same, whether a positive potential is given to the aluminum film or not. In other words, the direct attack of anions in the electrolyte does not explain the field-sensitive deterioration of photoresist adhesiveness. The most probable cause, then, is presumed to be the transport of anions inside the newly-formed oxide: some of them might move along the oxide-photoresist interface inward from the electrolyte under the influence of a strong electric field inside the oxide, breaking the bondage established between the aluminum and the photoresist.

The experiment and the subsequent argument have shown that photoresist is of satisfactory avail for the selective anodization of aluminum, only to the aluminum depth of about 1,000 Å at the most. (Let the obtained oxide be non-porous or porous.) In order to anodize aluminum to a deeper extent with desired portions of aluminum remaining unanodized, a secondary mask should be employed in place of photoresist, which should now serve as a primary mask for the former one. Considering that porous anodization satisfies the requirement of thick oxide formation, and that the deterioration of protective role of photoresist has been mainly attributed to its peripheral lift-up caused possibly by ion transport, the requirement for an ideal stop-off resist seems to be reduced to the following simple statement: it should be safe in an oxide-dissolving electrolyte, and its interface with aluminum should react anion inclusion in such a way that no substantial separation results at the interface. Besides these demands, it can be patterned using photoresist as a mask. These preliminary considerations suggest non-porous oxide as a possible candidate for a mask to porous anodization: it is compatible with photoresist work and anion inclusion at an interfacial area means nothing but new growth of porous oxide there. It has been demonstrated actually that non-porous oxide resists the growth of porous oxide if a forming voltage is lower than that of the former. But a further experiment has shown that the inevitable dissolution of the anodized oxide in the electrolyte acts to the disadvantage of the barrier. In some cases, the non-porous oxide gradually dissolves from its surface into the thickness which no longer resists the porous oxide growth in the long run. The barrier of composite oxide, on the other hand, is less vulnerable to the attack of the oxide-dissolving electrolyte, for it is embedded under the outer oxide skin.

4 Electromigration of Alumina-Coated Interconnections

In order to evaluate electromigration of aluminum interconnections with different alumina coatings, MTF (mean-time-to-failures) in hours was measured under the constant current density of $1.3 \times 10^5$ A/cm² and the operating temperature of 320±5°C. For the preparation of experimental samples, aluminum was deposited by electron beam evaporation to a thickness of 1.2 μ at the substrate temperature of 150°C on thermally grown SiO₂. Aluminum strips were then, formed by chemical etching, which underwent anodic oxidation. For the sample labelled as A, non-porous oxide formation was conducted in an ammonium borate electrolyte at the anodizing potential of 100 V.

For sample B, composite oxide formation was performed—porous oxide formation in 10% aqueous chromic acid at 10 V for 10 minutes was followed by subsequent anodization in an ammonium borate electrolyte at 100 V. For comparison with these alumina-coated samples, bare aluminum strips were also subjected to the experiment, and were labelled sample C. The result of this experiment and schematical cross-sectional views of three different aluminum strips are shown in Fig. 1.
5 Process Design

Taking into consideration the obtained experimental results combined with the available knowledge on anodization, a new process was designed for a highly reliable aluminum interconnect system of silicon integrated circuits. One typical example of such a process is explained in detail here (Fig. 2).

![Diagram of anodic aluminum structure](attachment:image.png)

<table>
<thead>
<tr>
<th>Wiring Structure</th>
<th>A</th>
<th>B</th>
<th>C</th>
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<tbody>
<tr>
<td>non-porous oxide</td>
<td>Al</td>
<td>Al</td>
<td>Al</td>
</tr>
<tr>
<td>composite oxide</td>
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Current density: $1.3 \times 10^6$ A/cm²
Operating temp.: $320 \pm 5°C$

Fig. 1 Mean time to failure of aluminum strips

5.1 Aluminum deposition
A silicon substrate with circuit elements yet to be processed for internal and external connections is uniformly covered with an aluminum film by a vacuum evaporation. Deposition by electron beam evaporation is more desirable than that from a resistance heated tungsten coil, for the possible inclusion of impurities from the tungsten coil into the deposited aluminum film. Anodic oxidation is quite sensitive to the purity of the aluminum film.

5.2 1st anodization
The entire surface of the aluminum film is now subjected to the 1st anodization to produce porous alumina at the applied voltage of $V_1$.

This 1st coating not only protects aluminum surface from chemical degradation or mechanical scratches at this stage, but it will play an important role at a later stage in forming a barrier of composite oxide. Another advantage resulting from this anodization is that photoresist adheres better to porous oxide surface than to aluminum.

5.3 Photoresist process
The surface of the porous oxide coating is then covered at those portions other than those used to form metallic connections with photoresist.

5.4 2nd anodization
Anodic oxidation is carried out in an oxide nonsolubing electrolyte at the positive potential of $V_2$, using the photoresist as a mask. $V_2$ should be close to the maximum value with which the photoresist endures in the electrolyte.

Composite oxide is thus formed on the surface of prospective aluminum interconnections. By this anodization, the silicon surface at the back side of the substrate is simultaneously anodized as well.

5.5 Removal of photoresist
Upon completion of the 2nd anodization, the photoresist is stripped off, using an appropriate chemical agent.

5.6 3rd anodization
Then, the wafer undergoes the 3rd anodization at the anodizing voltage of $V_3$ for the growth of porous oxide. If $V_3$ satisfies the condition of $V_1 < V_3 < V_2$, the 3rd anodization proceeds only at the portion which was not subjected to the 2nd anodization. The anodic conversion continues with constant current flow. In due time, interconnecting patterns make their appearance, the moment the anodizing current begins to decrease, which indicates the termination of the 3rd anodization. It might be suspected, unjustly, that a certain part of aluminum between adjacent interconnection lines might possibly remain unanodized. This means an electrical short circuit of the two lines, no matter how small an amount the unanodized aluminum might be left.

In such cases, however, the addition of continued anodization ensures the electrical separation of the
two interconnection lines as long as either one or both of the two are supplied with a positive potential by way of silicon contact windows.

By this anodization, there exists a slight increase of volume, resulting from the chemical conversion of aluminum into its oxide. However, any unevenness of the interconnection layer, attributable to this volume change is negligible as compared with that involved in the conventional device.

5.7 4th anodization

The 3rd anodization is followed by the 4th anodization to improve the reliability of this structure. The wafer is now subjected to the same treatment as the 2nd anodization, but in this case a higher positive potential is supplied. In this treatment, anodizing current flows through the porous oxide to fill the pores on aluminum. In consequence, aluminum interconnections are completely covered, on top and both sides, with the composite oxide. With this structure, aluminum has current-induced failure to the least degree.

5.8 Heat treatment

Heat treatment is conducted as the final stage of the anodic processing at an elevated temperature (450~500°C). This step not only ensures aluminum ohmic contact with silicon, but improves insulating characteristics of the anodized oxide.

6 Modification of the New Processing

For a satisfactory fabrication of a NPN discrete transistor, modification should be given to the standard processing described above in sequence, due to the fact that, at the stage of additional voltage application of the 3rd anodization, a collector-base junction is reversely biased at $V_{z}$ which is usually lower than $BV_{CEO}$. Under this circumstance, both emitter and base region have a floating potential. Therefore, anodization in the interelectrode area—the area between the emitter electrode and the base electrode—does not proceed satisfactorily if the outside of the base electrode is completely anodized earlier even by an instant. To overcome this difficulty, the 3rd anodization is preceded by the covering of photoresist over the outside region of the base electrode. The 3rd anodization is conducted upon the interelectrode area, to be terminated at the anodizing progress to a certain aluminum depth. The photoresist is, then, stripped off, and the 3rd anodization is resumed. By this arrangement, the inter-electrode area is anodized completely down to the bottom sooner than the outside base region. At the final anodizing stage in the former area, a positive potential is supplied from the outer region, while in the latter, it is from the substrate (by way of scribing windows). This modified version of the anodic processing is useul not only for NPN transistors but also for p-channel MOS devices.

7 Application of the New Structure to Various Devices

Standard discrete transistors of bipolar type were fabricated with the new anodic aluminum lead-outs. As a result, the improvement of $h_{fe}$ in low collector current region ($I_{C} \leq 100 \mu A$) was observed, in comparison with devices with the etched aluminum lead-outs. The result indicated the effectiveness of this passivated lead-out structure for low-frequency low-noise transistors. 2SC1222, which is a NPN transistor of this type, was actually processed with the anodic method, and proved the improved characteristic in low noise performance. Fig. 3 shows the $h_{fe}$ of this device as a function of collector current and the noise figure as a function of frequency. Another application was given to high voltage transistors.

![Graphs showing device characteristics of 2SC1222 (NPN), processed with anodic aluminum oxidation method](image-url)
8 Conclusion

A combination of photoresist technology and anodizing method has realized a new processing for a reliable structure of aluminum interconnections. The structural feature is that aluminum interconnect paths are covered, on top and both sides, with composite non-porous oxide, and that an entire surface of the interconnect layer is substantially flat. With this processing, the SiO₂ surface of the device is never exposed to an environmental atmosphere, which acts to the advantage of protection to contaminants from outside. The anodic film obtained by this processing is instrumental in improving various device characteristics of bi-polar and MOS transistors, presumably due to its passivation effect on SiO₂.

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7) M.J. Dignam, ibid. 105, 184 (1962).