- pp. 1587-1594 (1969), Proc. IEEE.
- 3) C.J. Santro, D.L. Tolliver, "Multilayer metallization for LSI", vol. 59 (No. 10), pp. 1403-1409 (1971), Proc. IEEE.
 - 4) E.D. Metz, "Metal problems in plastic encapsulated integrated circuits", vol. 57 (No. 9), pp. 1606-1609 (1969), Proc. IEEE.
 - 5) J.J. Bart, "The analysis of chemical and metallurgical changes in microcircuit metallization systems", vol. ED-16 (No. 4), pp. 351-356 (1969), IEEE Trans. Electron Devices.
 - 6) K.D. Kang, et al., "A Cr-Ag-Au metallization system", vol. ED-16 (No. 4), pp. 356-360 (1969), IEEE Trans. Electron Devices.
 - 7) J.R. Black, "Mass transport of aluminum by momentum exchange with conducting electrons", Proc. 1967, Ann. Symp. on Reliability Physics, IEEE Cat. 7-15c58, Nov. (1967).
 - 8) J.R. Black, "Aluminum conductor failure by mass transport", Proc. 3rd International Congr. on Microelectronics, Munich, Nov. (1968).
 - 9) J.R. Black, "Electromigration-a brief survey and some recent results", vol. ED-16 (No. 4), pp. 338-347 (1969), IEEE Trans. Electron Devices.
 - 10) S.M. Spitzer, S. Schwartz, "The effects of dielectric overcoating on electromigration in aluminum interconnections", vol. ED-16 (No. 4), pp. 348-350 (1969), IEEE Trans. Electron Devices.

Technical Paper

Glass Passivation of Silicon Devices by Electrophoresis

Kiyoshi MIWA*, Mitsuko KANNO*, Sadami KAWASHIMA*,
Susumu KAWAMURA** and Takehiro SHIBUYA**

A new deposition technique of glass films on the silicon surface by electrophoresis in which acetone, isopropyl alcohol or ethyl acetate is used as a suspension medium, and ammonium or hydrofluoric acid is used as an additive electrolyte has been investigated. The suspension in acetone with a little amount of hydrofluoric acid (0.0075 mol/l) is used to achieve uniform and fine glass deposition.

The glass characteristics of several ternary systems and the effects of additive constituents in zinc-borosilicate glass were also studied by means of differential thermal analysis, thermal expansion measurement and capacitance-voltage ($C-V$) measurement of Metal-Glass-Silicon (MGS) capacitor structures. The glasses in the system $ZnO-B_2O_3-SiO_2$ are suitable for deposition on the silicon substrate over a wide range of composition because of their thermal expansion coefficients matching that of silicon. Among the several additives in zinc-borosilicate glass studied in this paper, the addition of Ta_2O_5 in appropriate amount seems to stabilize the silicon surface. The dependence of voltage-current ($V-I$) characteristics of the glass-passivated silicon $p-n$ junction on the condition of firing was measured for some glasses. The oxygen content in the atmosphere of firing as well as the temperature plays an important role to raise the surface charge density toward positive direction.

1 Introduction

In recent years, glass films have been used for the surface passivation of semiconductor devices in order to obtain high reliability and to eliminate the need for the conventional hermetically sealed header. The use of glass films for surface passivation was first proposed by Perri, et al.,¹⁾ Langdon, et al.,²⁾ and Davis, et al.,³⁾. Another paper was later presented by Perri⁴⁾.

The techniques of depositing thin glass films on silicon substrates by sedimentation have been developed by Pliskin and Conrad⁵⁾. However, many other methods are available to form glass films such as RF

sputtering, vapor deposition, spraying, silk screening and electrophoresis. These methods except RF sputtering and vapor deposition contain the deposition stage of glass powder and the firing process of the deposited glass layer. The sedimentation by centrifuging is excellent to form controllable and uniform thin glass layer for conventional transistors and diodes, while the RF sputtering method is profitable for the devices which should not be heated at high temperature. The electrophoretic deposition, on the other hand, has many advantages such as; more rapid deposition rate, greater thickness, the simplest deposition equipment, capability of selective deposition by isolator films, simultaneous deposition on both faces of silicon wafers and the uniform glass thickness in the mesa grooves.

Studies on electrical characteristics of glass films

* Nippon Electric Co. (Kawasaki)

** Nippon Electric Glass Co. (Otsu)

by means of $C-V$ method were also presented by Kerr⁶⁾ for lead-alumino-borosilicates and zinc-alumino-borosilicates, by Snow and Dumesnil⁷⁾ for lead-borosilicates, and by Hewitt⁸⁾ for lead-borosilicates. However, few reports have been published for the characteristics of zinc-borosilicates. For applying thicker glass films on high voltage devices, it is most important to select an appropriate glass which has a thermal expansion closely matching that of silicon and has no ion drift in the glass layer.

The purpose of this paper is to describe experimental investigations on the following items.

1. Electrophoretic deposition method for glass passivation.
2. Effects of additive constituents into zinc-borosilicates on glass characteristics and on electric characteristics of glass films.
3. Device characteristics of the glass-passivated $p-n$ junctions by electrophoresis.

2 Experimental and Results

2.1 Electrophoretic deposition

For high voltage devices such as thyristors and triacs, rather thick films are needed and the formation of deep mesa grooves on both faces is necessary to obtain high voltage performance. The electrophoretic deposition of glass is a suitable technique for this purpose. Electrophoretic deposition of conducting materials such as graphite and metals has been investigated for many years. For example, that of Nb powder was reported by Gutierrez, et al.,⁹⁾ and the following materials have been deposited by this method; B, Dy, Au, Nb, Mo, W, Re, Nb₂Sn, ZrH₂, ThC, UC, NpC, Puc, (ZrU) C, UWC, UMoC₂, UO₂, Ta₂O₅, Al₂O₃, and some mixtures such as W-UO₂ and Mo-UO₂ composites. The deposition of barium titanate powder was also described by Lamb, et al.,¹⁰⁾. In this paper the glass deposition on silicon by electrophoresis was studied in some suspension media with additive electrolytes. The experiments were performed by using a plating cell shown in Fig. 1. The cell, made of a Teflon cylinder was equipped with suspension medium, glass powder, anode metals such as gold or platinum, and silicon substrates. Desired glass powder was mixed into the suspension medium (organic solvent), in which a little amount of electrolyte was added and agitated ultra-sonically to suspend the glass particles in near-colloidal state. The metal anodes and the silicon substrate were placed in this colloidal suspension and after several minutes the positive constant voltage was applied to the metal anodes, since most of glasses were charged positively in this system.

Fig. 1 Plating cell

Although the particle size of suspension was influenced by the viscosity and the dielectric constant of the suspension medium, it ranged usually from 1 to 20 microns as described later.

Acetone, isopropyl alcohol (IPA) or ethyl acetate was selected as a suspension medium after the trials of many other solvents. It is necessary for passivation of silicon surface that the glass films do not contain impurities and metal ions. Therefore, it is not desirable to add the electrolyte in the suspension medium. On the other hand the electrophoretic deposition could be made to form a stable and adherent deposit by the use of additives. As a result of checking many kinds of additives such as hydrofluoric acid, ammonium fluoride, ammonium, ammonium chloride, urea and fluoroboric acid for each suspension medium, ammonium and hydrofluoric acid were found most stable to make the deposition uniform and adherent.

The relation of the deposition rate vs. the molarity of additives is shown in Fig. 2 for #351 glass made by General Electric. Since other zinc-borosilicate glasses which were melted and tested by us had similar tendency for electrophoresis, GE # 351 glass was used in this experiment as a representative of zinc-

- 1: Acetone 133 V/cm, 2: IPA 133 V/cm
 3: IPA 300 V/cm, 4: Ethyl acetone 200 V/cm
 5: Acetone (NH₄OH) 133 V/cm

Fig. 2 Deposition rate vs. molarity of additive (49% HF) for GE # 351 glass (0.02 g/cc)

borosilicates. The molarity of additives at the maximum deposition rate was found to depend on the conductivity of solvents and the addition of HF showed rather steep peaks, while that of ammonium was found to give a flat plateau.

It was shown that the addition of ammonium was easy to be controlled, since the molarity was not critical to the deposition rate. However, the addition of HF made the deposited layer more uniform and more fine and dense.

The typical deposition rates for several suspension media containing HF vs. applied voltage are shown in Fig. 3. As the applied voltage increased, the deposition rate increased rapidly and then came to the saturation. As the applied voltage increased further, the deposition rate began to decrease gradually. The decrease with voltage increase was considered to be due to the convection of the solvent by the self-heating effect. The deposition in acetone was found to need the least voltage for the peak of deposition rate owing to the highest dielectric constant and the lowest viscosity.

Fig. 3 Deposition rate vs. plating field for GE #351 glass (0.02 g/cc)

Fig. 4 shows the relation of the weight of deposited glass vs. the plating time. It was found that the weight increase of the deposited glass reached a saturated value in 2~4 minutes and decreased after 4 or 6 minutes. This decrease with time was probably caused by the running effect in solvent. After the deposition of glass layer in a certain thickness the glass particles in the outer surface region of deposited glass had poor bonding strength and were easily swollen and dropped off.

The suspension for this experiment was 325 mesh-passed glass powder and the concentration of glass in suspension was 0.02 g/cc, but if more milled glass was used it was not necessary to use such a high

Fig. 4 Weight of deposited glass vs. plating time for GE #351 glass (0.02 g/cc)

concentration.

The distribution of particle size for electrophoretically deposited glass is shown in Fig. 5. The maximum particle diameter was found to be about 20 microns, and the median diameter was about 6 microns. These results agreed exactly with the early work reported by Gutierrez, et al.,⁹⁾

Fig. 5 Distribution of particle size for deposited glass

Of course, it is necessary to avoid mixing impurities such as sodium or water into the suspension, because these impurities lead the abnormal deposition.

2.2 Effects of additive constituents into zinc-borosilicate

After the investigation of the differential thermal analysis (DTA) and the thermal expansion coefficient measurement for several glass systems such as $\text{ZnO-B}_2\text{O}_3\text{-AlPO}_4$, $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$, and $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$, we selected $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ system for the passivation

glass, since it had the lowest thermal expansion matching that of silicon and wide range of glass formation.

This zinc-borosilicate glass generally had two crystallization peak in DTA curve, and were found the fine crystals of willemite ($2\text{ZnO}\cdot\text{SiO}_2$) at the first peak and the fine crystals of zinc-borate ($\text{ZnO}\cdot\text{B}_2\text{O}_3$) at the second peak by the electron diffraction analysis.

In order to study the influence of additives in this system, ZnO (62.5 wt%), B_2O_3 (27.5 wt%), SiO_2 (10.0 wt%) was chosen as the base material, and Ta_2O_5 , CeO_2 , Sb_2O_3 and PbO were used as the additive constituents.

Fig. 6 shows the effects of these additives on crystallization temperature, in which the horizontal axis indicates the addition ratio to 100 parts of the base glass. The addition of Ta_2O_5 made the crystallization peak in DTA curve higher, but it showed two crystallization peaks above 5 wt%. The lower peak of them was appeared at considerably low temperature.

The addition of CeO_2 did not change the crystallization temperature remarkably, while that of PbO caused to lower it. In the case of Sb_2O_3 , the crystallization temperature rose at first and it dropped down gradually above 1 wt%.

Base; ZnO : 62.5, B_2O_3 : 27.5, SiO_2 : 10 wt%

Fig. 6 The effects of additives on crystallization temperature (T_c)

The effects of additives on thermal expansion coefficients are indicated in Fig. 7. The thermal expansion coefficient was raised by the addition of CeO_2 , Sb_2O_3 and PbO , but was not changed by that of Ta_2O_5 .

The etching rates of these glasses by 49% HF were studied and are shown in Fig. 8, from which most

additives except Sb_2O_3 are considered to be able to make the glass networks denset. The effects of additives on dielectric strength are shown in Fig. 9.

Fig. 7 The effects of additives on thermal expansion coefficient (α)

Firing condition; 700°C 1 hr + 750°C 20 min in O_2

Fig. 8 The effects of additives on etching rate in 49% HF

Firing condition; 700°C 1 hr + 750°C 20 min in O_2

Fig. 9 The effects of additives on dielectric strength (E_B)

Fig. 10 shows the data of surface charge density (N_{FB}) as a function of weight percentage of additives. The surface charge density is calculated from the measured C - V curves of Metal-Glass-Silicon (MGS) diode structures in firing condition of 750°C for 20 minutes after prebake at 700°C for 1 hr. It was found that Ta_2O_5 brought N_{FB} positive and PbO did not change N_{FB} , while Sb_2O_3 raised N_{FB} in negative direction. In this paper, we define that the positive N_{FB} means the positive V_{FB} , that is, the negative oxid charge. The addition of CeO_2 also raised the surface charge density in negative direction remarkably in the concentration range up to 2 wt%, and then started to decrease it above that concentration.

Fig. 10 The effects of additives on surface charge density (N_{FB})

In the case of glasses fired at lower temperature, the surface charge density was not changed extremely, but the impurity ions contained in the glass layers were easy to drift by bias-temperature (BT) treatments, since the structure of glass networks were considered to be less dense.

The C - V shifts of those glasses are shown in Fig. 11 for the weight percentage of additives, which were calculated from C - V curves of MGS structures before and after BT treatments. The addition of CeO_2 caused a large drift of ions, and that of Ta_2O_5 made the glass films most stable especially at 5 wt%. Sb_2O_3 and PbO were thought to be in the glass network above 3 or 4 wt%, since these C - V shifts decreased and were stabilized above it.

Fig. 11 The effects of additives on C - V shift by BT treatments (150°C, 100 V, 17 hrs)

2.3 Device characteristics of the glass-passivated p - n junction by electrophoresis

GE #351 glass was deposited by electrophoresis on silicon p - n junctions which were made on 15~30 ohm-cm N -type silicon substrates by diffusion process and were grooved in mesa type to be 2 cm × 2 cm pellets.

The influence of the oxygen content in firing atmosphere for the deposited glass on the electric characteristics of silicon p - n junction is shown in Fig. 12. The content of oxygen is found to be important for the reverse current and breakdown voltage. From the facts that the electric characteristics of diodes fired in oxygen atmosphere were better than those in N_2 atmosphere, we used oxygen in the following experiments as an atmosphere of firing. The temperature and the time of firing affect the device characteristics as well. As the temperature increased, the breakdown voltage increased slightly in the range of temperature up to 750°C, and the reverse current also increased with the temperature. The time of firing was not so critical for the breakdown voltage, but the reverse current increased with the time of firing as shown in Fig. 13. Surface charge densities of several zinc-borosilicate glasses are shown in Fig. 14 as a function of the temperature. In this figure, all glasses have the tendency of increasing N_{FB} with

Fig. 12 The effects of firing condition (atmosphere) on V-I characteristics and surface charge density (N_{FB}) at room temperature (25°C)

Fig. 13 V-I characteristics of glassivated Si p - n junction at room temp. (25°C) vs. firing time

the temperature of firing above a certain temperature. Below this temperature, the data are much scattered and have large variation.

In connection with the observation of the photographs of these glasses by polarizing microscope, positive surface charges were considered to be associated with the number of fine crystals in the glass layer. V-I characteristics of glass-passivated p - n junctions for several glasses at room temperature are shown in Fig. 15 as a function of firing temperature. The characteristics at elevated temperature also showed a similar tendency.

Fig. 14 Surface charge density of MGS diode vs. firing temperature

Fig. 15 V-I characteristics of glassivated Si p - n junction at room temp. (25°C) vs. firing temperature

For the correlation between V-I characteristics and the surface charge density, the empirical results showed that the V-I characteristics for N type substrates became better in the case of positive surface charge.

3 Discussion

Electrophoretic deposition of glass films in the suspension medium of acetone, in which a little amount of HF was added was done successfully on the silicon p - n junction which was grooved in mesa type structure. There was a strong suspicion that the use of HF might change the glass characteristics remarkably,

because HF dissolves most of glasses. As a result of many considerations, the surface charge density of MGS capacitor which was deposited by this method was smaller and more stable than that made by sedimentation, while the C - V curve for the capacitor made by sedimentation had the injection-extraction type hysteresis in it. Although a little effect of HF for glass characteristics was found in glass transformation temperature and the glass particles were considered to be dissolved to some extent, the devices passivated by this method had a very high quality. The most important point, however, is that the glass layer deposited by electrophoresis should be baked at the temperature below the softening point prior to firing in order to remove the electrolyte absorbed on the surface of glass particles.

In the glass system of zinc-borosilicates, excess atoms which did not participate in glass networks, such as CeO_2 , Sb_2O_3 , PbO and Ta_2O_5 , were seemed to be mobile at high temperatures from the experimental data described above. We calculated the activation energies from the Arrhenius plots of C - V shift after BT treatment in the temperature range from 150 to 210°C, and found that the activation energies for the glasses added Sb_2O_3 , PbO and Ta_2O_5 were 0.58, 0.86 and 0.98 eV, respectively, in this system. The activation energy for the glass to which CeO_2 was added could not be determined because of the large shift at high temperatures. Therefore, we surmise that the addition of Ta_2O_5 makes the glass layer stable and improves the device characteristics, and the small addition of Sb_2O_3 causes high dielectric strength of the glass film.

As described before, the positive surface charge were desirable to improve the characteristics of the p - n junction for N type substrates which were covered with the glass, and it might depend on the number of fine crystals in the glass. Hence it is hopeful that the addition of the constituents nucleating in the glass brings the surface charge to positive direction. In the experiment of firing condition, we found that the oxygen content of atmosphere was very important to improve the V - I characteristics, and that ozone was better than oxygen as a constituent in atmosphere. We consider that the defects of oxygen in the glass cause negative charge on silicon

surface, and the fine crystals cause positive charge on it. However, the excess crystallization results in the degradation of V - I characteristics owing to the grain boundaries of crystals. Therefore, it is desirable to fire the glass layer at the temperature below the crystallization peak, at which the glass layer contains the fine crystals to some extent.

4 Conclusion

The electrophoretic deposition of glasses can be adapted to coat the surface of the silicon p - n junction. Especially the deposition in acetone, in which 0.0075 mol/l of HF is added, shows splendid accomplishments.

Among several glass systems, $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ has a suitable thermal expansion coefficient closely matching that of silicon and its passivation effect can be improved by addition of about 5 wt% Ta_2O_5 and some nucleating materials. The electrical characteristics of the p - n junction coated with these zinc-borosilicate glasses depend remarkably on the atmosphere, the temperature and the time of firing of the glasses. Oxygen atmosphere makes these glasses electrically stable and makes the surface charge density positive.

Acknowledgment: The authors would like to acknowledge the continuing guidances and encouragements of Dr. Y. Moriguchi and Dr. K. Takagi. We also would like to thank Mr. H. Hattori for his helpful discussions. (Received Dec. 28, 1971)

Reference:

- 1) J.A. Perri, H.S. Lehman, W.A. Pliskin, J. Riseman, "Surface Protection of Silicon Devices with Glass Films", presented to the Electrochemical Society at Detroit, Michigan, Oct. 2, (1961).
- 2) J.L. Langdon, W.E. Mutter, R.P. Pecoraro, K.K. Schuegraf, "Hermetically Sealed Silicon Chip Diodes and Transistors", presented to the 1961 Electron Devices Meeting, Washington, D.C., Oct. 27, (1961).
- 3) E.M. Davis, W.E. Harding, R.S. Schwartz, "Solid Logic Technology: Versatile, High Performance Microelectronics", IBM Journal **8**, p. 102, April, (1964).
- 4) J.A. Perri, "Glass Encapsulation", SCP and Solid State Tech. p. 19 (1965).
- 5) W.A. Pliskin, E.E. Conrad, *Electrochem. Technol.* **2**, 196 (1964).
- 6) D.R. Kerr, *IBM Journal* **8**, 385 (1964).
- 7) E.H. Snow, M.E. Dumesnil, *J. Appl. Phys.* **37**, 2123 (1966).
- 8) M. Dumesnil, R. Hewitt, *J. Electrochem. Soc.* **117**, 100 (1970).
- 9) C.P. Gutierrez, J.R. Mosley, T.C. Wallace, *ibid.* **109**, 923 (1962).
- 10) V.A. Lamb, H.I. Salmon, *Ceramic Bulletin* **41**, 781 (1962).