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Effect of Utilizing Hydrogen-Treated Tantalum Anodized Oxidation on Symmetry of Current–Voltage Characteristic of Metal–Insulator–Metal Element

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The symmetry of current–voltage (I–V) characteristic of the metal–insulator–metal (MIM) element with the insulator of tantalum anodic oxidation TaO_x which is heat-treated in hydrogen (hydrogen-treated) is greatly improved. Meanwhile, the symmetric I–V characteristic, unlike that of the conventional MIM element with tantalum anodic oxidation TaO_x which is heat-treated in vacuum (vacuum-treated) or in an oxygen atmosphere, is independent of the choice of top-electrode material. In addition, the making process of the MIM element with hydrogen-treated TaO_x film is less than that of the conventional MIM element with vacuum-treated TaO_x film. Considering the oxide layer structure, we present a novel p–n$^-$–n band model for MIM element to explain these experimental phenomena.

KEYWORDS: metal–insulator–metal element, hydrogen-treated, vacuum-treated, p–n$^-$–n band model, thin-film diode

1. Introduction

Active-matrix addressing liquid-crystal displays (AMLCDs) are now widely used in many applications. Among various AMLCDs, the metal–insulator–metal type thin-film diode LCDs are thought to be preferable in comparison with thin film transistor (TFT) LCDs due to the simpler structure, less cost and higher aperture of about 80%. However, there still remain a few serious problems in metal–insulator–metal LCD (MIM-LCD). Among them, the afterimage phenomenon which is caused by the asymmetric current–voltage I–V characteristic of the MIM switching element is a big problem.[1] In order to solve the problem, the symmetry of the MIM I–V characteristic must be improved.

The MIM element has a tantalum oxide (TaO_x) layer between the top-electrode and the bottom-electrode. The I–V characteristics of the MIM elements follow the Poole-Frenkel effect,[2] which is strongly based on the property of the TaO_x layer. Therefore, the MIM I–V characteristics are affected by the formation conditions of the oxide layer. Normally, the TaO_x layer of MIM element was made by anodic oxidation of patterned Ta and then heat-treated in vacuum or in an oxygen atmosphere. Usually the conventional MIM element with this kind of oxide layer has asymmetric I–V curve and the I–V characteristic depends on the choice of top-electrode material.[3]

Considering several technological conditions, we found that the heat-treatment condition of the anodic oxide TaO_x was important. This paper originally presented that the MIM element with the anodic oxide TaO_x which was heat-treated in hydrogen atmosphere showed symmetric I–V curve which was independent of the top-electrode material. Considering the oxide layer structure, the authors proposed a novel p–n$^-$–n band model to give the explanation of the experimental phenomena.

2. Experimental

A cross-section view of the MIM element was shown schematically in Fig. 1. An etch-stop layer was prepared by sputtering Ta_2O_5 on a glass substrate. The MIM element included two metal layers of Ta and the top-electrode metal (Cr, Ta and Cu were used as top-electrode in experiments), which were formed by the sputtering method. The tantalum oxide layer (TaO_x) was formed by anodic-oxidation of patterned Ta. The anodic-oxidation was accomplished by the following conditions; the electrolyte solution was 0.01 wt% ammonium borate solution, anodizing voltage was 35 V and the counterelectrode was Pt plate (The set-up for anodic oxidation was shown in Fig. 2). After anodization, the anodic oxide TaO_x was annealed in vacuum at 420°C for 1.5 h or in hydrogen atmosphere at 330°C for 0.5 h. At last, the whole element was annealed at 300°C for 1 h (The last process is necessary only for the MIM elements with the vacuum-treated TaO_x layer).

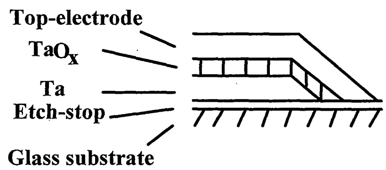

Fig. 1. Cross-section view of MIM element.

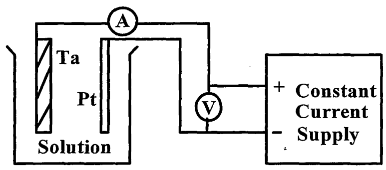

Fig. 2. Setup for anodic oxidation.

The current–voltage characteristics of MIM elements were measured by light-spot galvanometer SG-701-S and computer. The anodic oxide TaO_x property was investigated by Auger electron spectroscopy (AES).

3. Results

3.1 *I–V characteristics of MIM element with anodic TaO_x film which is heat-treated in vacuum*

Figure 3 shows I–V characteristics of MIM elements

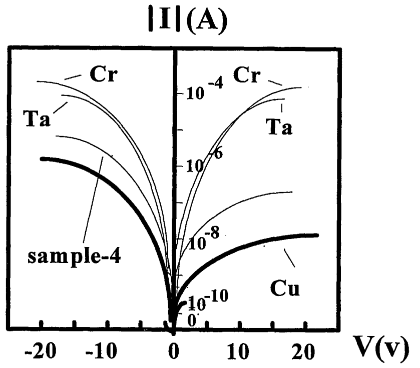

Fig. 3. *I–V* characteristics of MIM elements with vacuum-treated anodic oxide TaO_x film as insulator.

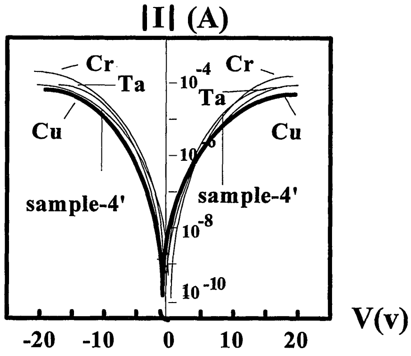

Fig. 4. *I–V* characteristics of MIM elements with hydrogen-treated anodic oxide TaO_x film as insulator.

with anodic oxide TaO_x which is heat-treated in vacuum at 420°C for 1.5 h. The *I–V* characteristics can be divided into two types (symmetric and asymmetric cases). In the case of adopting Ta or Cr as top-electrode, *I–V* characteristics of MIM elements are symmetric; in the case of adopting Cu as top-electrode, *I–V* characteristic is asymmetric. In addition, the *I–V* characteristic of sample-4 (Ta is used as top-electrode) whose process is the same as that of the conventional MIM element except that the whole element isn't annealed, is also asymmetric.

3.2 I–V characteristics of MIM elements with anodic oxide TaO_x film which is heat-treated in hydrogen atmosphere

Figure 4 shows *I–V* characteristics of MIM elements with anodic oxide TaO_x which is heat-treated in hydrogen atmosphere at 330°C for 0.5 h. From Fig. 4 the *I–V* characteristics of these elements are symmetric which are independent of the choice of top-electrode material (whatsoever for Cr, Ta or Cu) and the condition that the whole element is annealed or not. (The experimental conditions of sample-4′ are the same as those of sample-4 expect the making process of TaO_x layer.)

4. Discussion

From Figs. 3 and 4, the MIM elements with hydrogen-treated anodic oxide TaO_x show symmetric *I–V* characteristics. Considering the oxide layer structure, we explain it as follows.

The conventional Poole-Frenkel equation which describes the *I–V* characteristic of MIM element is shown as follows,[4]

$$I = \alpha V \exp(\beta\sqrt{V}) \tag{1}$$

with

$$\alpha = \frac{en\mu}{d}\exp\left(-\frac{\varphi}{KT}\right) \tag{2}$$

$$\beta = \frac{1}{kT}\left(\frac{e^3}{\pi\varepsilon_i\varepsilon_0 d}\right)^{\frac{1}{2}} \tag{3}$$

where I and V are current and applied voltage, respectively, and α and β are the parameters which are independent of the applied voltage. From eq. (1) it is apparent that the *I–V* characteristic of the MIM element is symmetric when the electric field is applied in different directions. However, the characteristics measured in experiments are asymmetric for some occasions (see Fig. 3), which indicates that the asymmetry of *I–V* characteristic of MIM element can't be described accurately by conventional Poole-Frenkel equation.

In order to determine the reason of the asymmetry and why MIM element with hydrogen-treated anodic oxide TaO_x layer shows good *I–V* characteristics, the analyses for the insulator layer are necessary because the Poole-Frenkel equation is strongly based on the property of this layer.

In fact, the Poole-Frenkel equation is deduced for insulator with perfect surfaces and interfaces, whereas an amorphous tantalum oxide film produced by anodization of the Ta layer is usually used as insulator in experiments. Figure 5 shows the in-depth atomic profiles obtained by AES with the surface-sputtering method for the MIM element in our experiments. From Fig. 5 a p–n^-–n structure with two junctions can be formed in the film, which bases on the following facts; In the region between the bottom-electrode Ta layer and the oxide layer, the oxide can dissolve excised metal atoms, so the oxide adjacent to the metal Ta becomes n-type. When the film is heat-treated in oxygen or in vacuum, the oxide layer becomes n^--type due to some donor levels are created (compared with the above n-type).[4] During the process of anodization, the concentration of adsorbed oxygen ions at the oxide surface is very high, the region is p-type. Thus, a p–n^-–n band structure is formed, which is shown in Fig. 6. Because the p-type, n^--type and n-type exist in the element, two junctions appear in the oxide layer; one of which is p–n^- junction near the top-electrode, and another of which is n^-–n junction near the bottom-electrode. Usually the internal voltage of the n^-–n junction on the right is much lower than that of the p–n^- junction on the left, so the influence of the n^-–n junction may be negligible.

The reason that the asymmetry of the *I–V* curve can't be described accurately by Poole-Frenkel equation is just because the influence of the p–n^- junction in the oxide film isn't considered in the equation. According to this, we present the p–n^-–n band model for MIM element to explain the asymmetry of *I–V* characteristics and the above experimental results.

The reason of asymmetry of *I–V* characteristics is explained as follows: When an external voltage v_f is applied

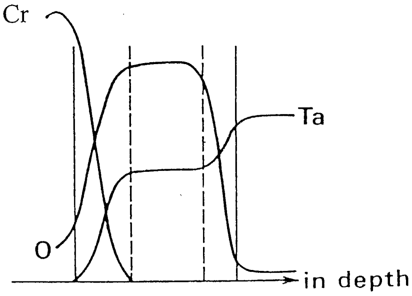

Fig. 5. In-depth atomic profiles obtained by AES with the surface-sputtering method for the MIM element.

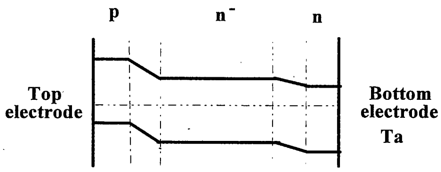

Fig. 6. p–n$^-$–n junction band model.

between two electrodes of the element and if the internal voltage of the p–n$^-$ junction is v_0, the total electrostatic potential variation across the junction is given by $(v_0 - v_{ff})$ for the forward bias voltage v_{ff} applied on the junction (from top-electrode to bottom-electrode) and by $(v_0 + v_{fr})$ for the reverse bias voltage v_{fr} applied on the junction (from bottom-electrode to top-electrode). How this comes about in the concrete in Fig. 7. When an electric field is applied to the MIM element in different directions, the effect of the electric field of the junction is different and the I–V characteristic of the element, therefore, shows asymmetry.

On the other hand, the internal electric field of the p–n$^-$ junction depends on the density of the acceptor impurity in the p-type region. When the density decreases, the potential barrier of the p–n$^-$ junction becomes lower, the screened effect of the internal electric field weakens and the symmetry, therefore, is improved. Oxygen is one of most important acceptors in the p-type region. If the density of oxygen in the p-type region decreases, the symmetry of I–V characteristic of MIM element is improved. For anodic oxide TaO_x which is usually heat-treated in vacuum or in an oxygen atmosphere, one method of reducing the density of oxygen in the surface of the film is to choose weak electronegative metal as top-electrode because it is easy for them to react with oxygen during the heat-treatment processes. So when weak electronegative metal is used as top-electrode and heat-treated at a certain temperature (If the element isn't annealed after sputtering the top-electrode, the I–V characteristic is also asymmetric even if the weaker electronegative metal is chosen, see sample-4 in Fig. 3), the symmetry can be improved according to the above analyses, which just explain the experimental results in Fig. 3. In fact, the electronegativity is lower than or equals to 1.6 for Ta and Cr; whereas the electronegativity equals to 1.9 for Cu. Moreover, coincidence between the above explanation and the Hirai's experimental results about the I–V characteristics of MIM element dependence on the top-electrode materials[4] is quite good.[5]

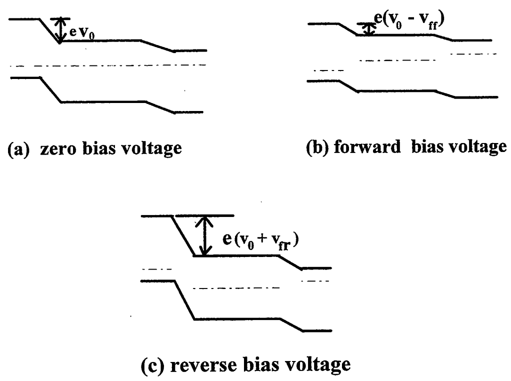

Fig. 7. The band diagram dependence on the bias voltage.

Certainly when the anodic oxide TaO_x is heat-treated in hydrogen atmosphere at a certain temperature (not in vacuum or in an oxygen atmosphere), the oxygen in the surface of the film reacts with hydrogen and the density of oxygen is also reduced, which is benefit to improve the symmetry according to the above analyses. Meanwhile, the symmetry is also independent of the top-electrode material because the density of oxygen in the surface is already reduced by hydrogen-treatment, which also reduces the last heat-treatment process for the whole element. These experimental results are shown in Fig. 4.

From the above experimental results it is apparent that the symmetry of I–V characteristics is improved in large when the potential barrier of the p–n$^-$ junction becomes lower, which also indicates that the influence of the n$^-$–n junction in this band model can be negligible.

5. Conclusion

We proposed and testified that using the hydrogen-treated anodic oxide TaO_x layer instead of the conventional vacuum-treated anodic oxide TaO_x layer, the MIM element has symmetric I–V characteristic which is independent of the choice of the top-electrode material. Meanwhile it can simplify the working process. In addition, considering the oxide structure, we propose a novel p–n$^-$–n band model to explain these experimental phenomena.

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1) H. Morita, K. Tadokoro, S. Kamagami, K. Sunohara, T. Iizuka and Y. Abe: Tech. Dig. Japan–Korea Joint Symp. Information Display (1991) p. 107.
2) H. Morita, K. Ishizawa, M. Shibusawa, Y. Tanaka and K. Inoue: *Proc. 10th Int. Display Research Conf., Amsterdam, 1990* (VDE-Verlag, Berlin, 1990) p. 200.
3) T. Hirai, K. Miyake, T. Nakamura, S. Kamagami and H. Morita: Japan Display'92, 1992, p. 229.
4) H. Matsunoto, A. Suzuki and T. Yabumoto: Jpn. J. Appl. Phys. **19** (1980) 71.
5) H. W. Liu, J. X. Yuan, J. F. Yuan, K. Ma and X. M. Huang: Proc. SPIE **2892** (1996) 107.