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Development of thin film getters for field emission display

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Abstract – For a high efficient field emission display (FED), the specific vacuum conditions below 10^{-7} Torr should be required. However, because the FED has the geometrical restriction due to its micro size, the thin film getters can be proposed for chemical pumping as a way to reduce impurity gases in the panel. The thin film getters, developed by employing the coating of new materials such as Ni or Pt on getter surface, can be used without any activation process and show the enhanced sorption characteristics. Especially, using the Zr (1 μm) thin film getters with the Pt surface layer, the significant gettering for various active gases could be achieved from 9×10^{-5} Torr to 1×10^{-6} Torr or below. This good sorption properties is mainly contributed to the surface coating layer which shows the catalytic effect for gas dissociation and protects the getter materials against oxidation.

I. Introduction

Field emission display (FED), using the technology of vacuum microelectronics, should meet the specific vacuum conditions below 10^{-7} Torr in order to achieve a high efficiency-panel. Hydrogen is the main residual component in a general ultra-high vacuum environment, however, recently, the dominant impurity gas of the actual FED panel is reported by water vapor [1, 4]. In addition, oxygen, carbon monoxide, carbon dioxide, and methane exist with their small partial pressures [2-4]. These impurity gases, generated by outgassing from glasses, electric components, and phosphors through thermal heating process and electron bombardments, degrade the emission efficiency and shorten the lifetime of device. B. R. Chalamala *et al.* [4] showed the experimental results that oxygen containing gases caused the significant degradation of electron emission from Spindt type cathode due to the Mo oxide formation on the surface. In addition, the current stability was not certified in poor vacuum, because the adsorbate on field emitters changed the work-function of cathode easily. Consequently, the control of impurity gases in the panel is a critical issue for the performance and lifetime of FED.

However, there is a limitation in achieving the sufficient vacuum condition of panel by the mechanical pumping during packaging process, because flat panel display such as FED has the micro-sized panel gap between face and base plate. In order to overcome these problems, the getters for chemical pumping could be proposed as a way to reduce impurity gases in the panel.

Various types of getters are used according to their application usage, for example, Ba evaporable getter (EG) for cathode-ray tube (CRT) [5-6] and non-evaporable getter (NEG) for lamp [7], particle accelerators [8-9], and electron tube [10], *etc.* These traditional getters, however, are not easy to apply to the FED panel, because those should require a high flashing temperature for Ba evaporation and a thermal activation process for surface oxide removing on NEGs, respectively. In addition, those need a back chamber for getter loading due to its deposition and bulky size, respectively.

Therefore, as a solution to the easy appliance of getters for FED, we developed the thin film getters that could be used without any activation process and showed the enhanced sorption properties employing the coating of new materials such as Ni or Pt. These materials show the catalytic property for hydrogenation and protect getter material from the oxidation during handling process. This paper will characterize the role of surface layer on thin film getters and the basic sorption properties for various

active chemical gases such as hydrogen, oxygen, carbon monoxide, carbon dioxide, and water vapor.

II. Experimental

Getter materials chosen in this study are the elements of the column IV A of the periodic table, i.e. Zr, or Ti. These materials have a good chemical affinity and a large solubility for various chemically active gases. In order to remove the activation process, the Ni or Pt are coated on getter materials. These materials play an important role in fast dissociation of gas molecule and protection against oxide formation on getter materials, because of their low activation energy for the dissociation of gas molecule and low absolute value of heat of oxide formation, compared to Zr and Ti. The thin film getters were fabricated by sequential coating of getter with 1μm thickness and catalytic material with 10-40 nm thickness on flat SiO_2 (200 nm)/Si and rough alumina substrates, using D. C. magnetron sputtering system.

Gas sorption properties at the pressure range from 10^{-7} to 10^{-4} Torr were obtained by a modified volumetric Siverts' apparatus [11]. The apparatus, which had the total volume of 140cc, was evacuated by turbo molecular pump backed with rotary pump and the residual pressure was routinely below 2×10^{-7} Torr. The samples used for sorption characterization had the 5 cm × 5 cm × 1 μm geometry and did not go through any thermal activation before gettering test. Gas flow was controlled by a micro-variable leak valve at a pressure range from 9×10^{-6} to 9×10^{-5} Torr. The pressure change resulting from gas absorption was detected in a range from 10^{-7} to 10^{-4} Torr by a cold cathode gauge in the closed system.

III. Results and Discussion

Fig. 1 is the scanning electron microscope (SEM) view of Ni(10 nm)/Zr(1 μm) thin film getters deposited on the substrates with different surface roughness. The morphology of thin film getters in Fig. 1 (a) and (b) is not contributed to surface layer but the overall layer including getter material. The thin film getter deposited on alumina substrates with the roughness of 0.1 μm variation was somewhat porous and groovy, while a dense and flat film was

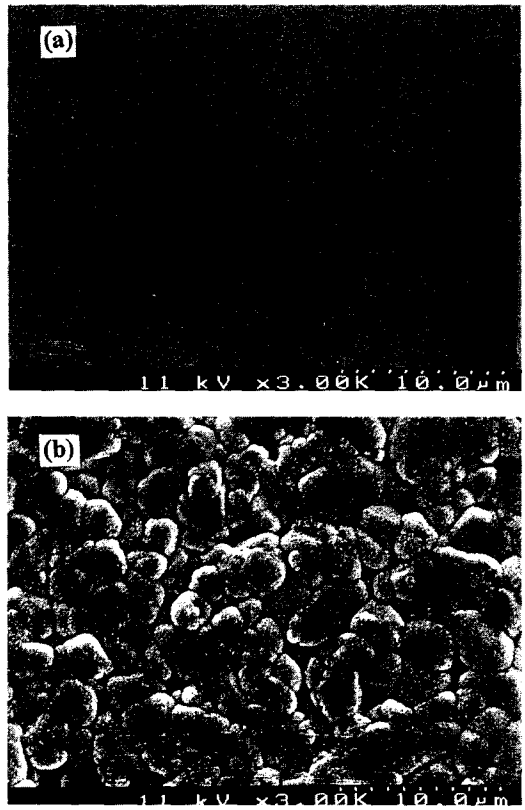

Fig. 1. Surface morphology of the film getters SiO_2/Si substrate (b) Alumina substrate.

obtained on SiO_2/Si substrate. This difference of surface morphology makes a change in total surface area and finally has an effect on the sorption kinetics. Fig. 2 shows the hydrogen sorption curves with Ni(10 nm)/Zr thin film getters deposited on different substrates. The absorbed quantity into the

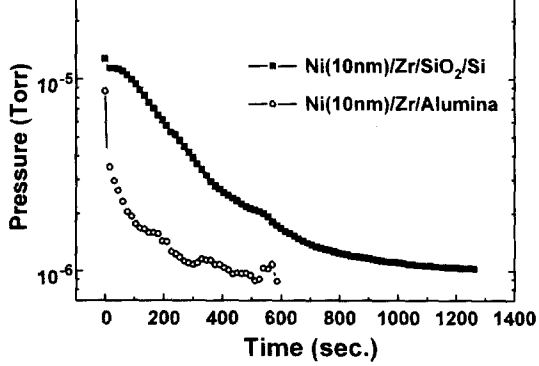

Fig. 2. Effect of substrate for hydrogen absorption.

getters was almost same due to very low partial pressure. The thin film getters on alumina substrate showed much better sorption performances due to the relatively higher active surface area, because the surface morphology of thin film getters influences the hydrogen sticking factor [12]. Therefore, the increase of surface roughness of thin film getters is a one way to enhance the sorption kinetics and the thin film getters with porous morphology will be used much effectively in the actual panel.

Sorption kinetic results obtained for different thickness of catalytic layer under same hydrogen pressure conditions have been plotted in Fig. 3. In the case of Ni catalyst shown in Fig. 3(a), as the thickness of Ni layer was increased, the hydrogen sorption kinetics were enhanced. These different sorption rates according to Ni thickness might be contributed to the degree of oxygen contamination in the film, which came from air exposure during getter handling process. Oxygen composition, confirmed by XPS depth profile analysis, is highest in the film with 10nm Ni thickness and it is slightly decreased as the Ni thickness increases. Therefore, the poor sorption kinetics of Ni(10 nm)/Zr getters is due to the reduction of hydrogen sticking probability by the existence of oxygen atoms on the surface of getters. On the other hand, for the Pt catalyst shown in Fig. 3(b), the sorption kinetics showed dissimilar results that the thin film getter with 20 nm Pt thickness showed better sorption kinetics than that with 40 nm Pt thickness. It means that the thickness is not a critical factor for Pt catalysis due to its noble metal property. In XPS depth profile of Pt/Zr getters, oxygen contamination, irrelevant to their thickness, was scarcely observed. Consequently, at least the 20 nm thickness of catalytic layer should be required to obtain a good sorption property and protect getter materials against oxidation from an air exposure.

Fig. 4 shows the influence of the getter materials for hydrogen absorption. Zr, Ti and some alloys based on them have been used as bulk getter materi-

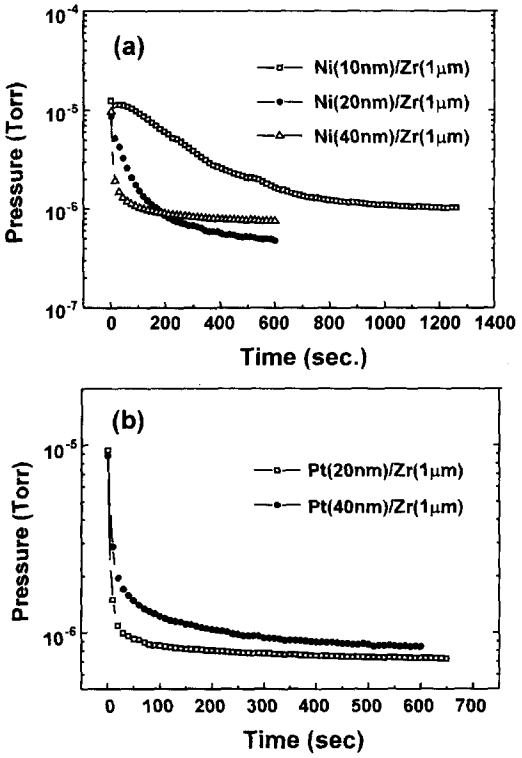

Fig. 3. Effect of the thickness of catalysis on hydrogen absorption Getters with Ni catalysis (b) Getters with Pt catalysis.

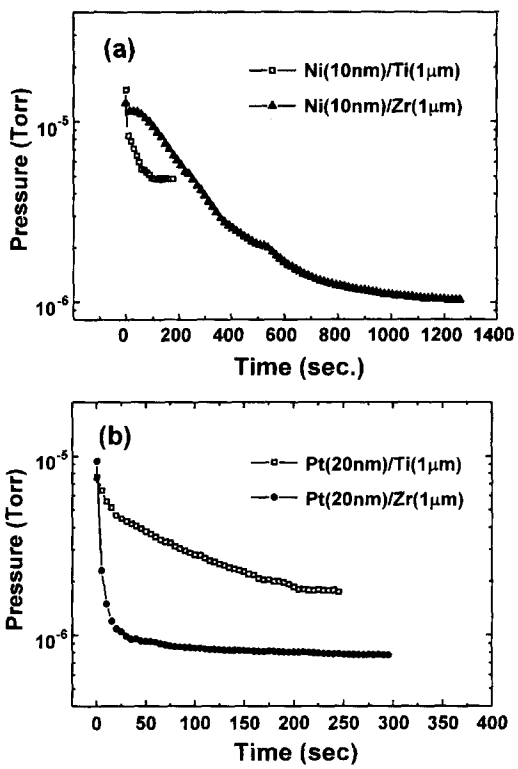

Fig. 4. Effect of getter materials on hydrogen absorption Getters with Ni catalysis (b) Getters with Pt catalysis.

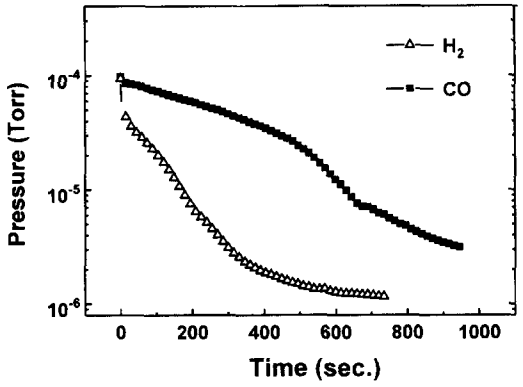

Fig. 5. Sorption properties of Ni(40nm)/Zr(1 μm) getter at the pressure range of 10^{-5}Torr.

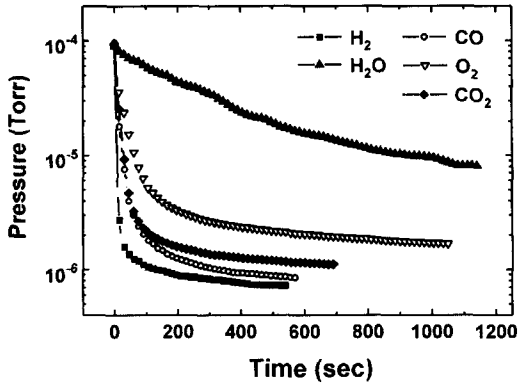

Fig. 6. Sorption properties of Pt(20nm)/Zr(1 μm) getter at the pressure range of 10^{-5}Torr.

als because these metals have a great affinity for various chemically active gases such as oxygen, nitrogen, hydrogen, carbon monoxide, and some hydrocarbons. Regardless of the species of catalytic materials shown in Fig. 4(a) and (b), the absorption results for hydrogen obtained showed that the gettering property of Zr getters was superior to Ti getters for hydrogen absorption at very low pressure. It is not clear why Zr getters show larger hydrogen sorption capacity but it might be due to larger hydrogen solubility of Zr than that of Ti at room temperature.

Fig. 5 showed the results of sorption properties for hydrogen and carbon monoxide, using Ni(40 nm)/ Zr(1 μm) thin film getters, respectively. Comparing the absorption kinetics of carbon monoxide with hydrogen, the sorption rate of carbon monoxide was significantly reduced at the gas pressure of 10^{-5} Torr range. This is particularly evident in the case of sorption of active gases except hydrogen where the bulk diffusion plays an important role in the sorption kinetics, while in case of hydrogen, which easily diffuses even at room temperature, such an effect appears to be less noticeable. These poor sorption characteristics for carbon monoxide can be improved by increasing the getter temperature to enhance the diffusion of the sorbed gases.

Fig. 6 showed the sorption characteristics of Pt(20 nm) / Zr thin film getters for various active gases. Using the Pt(20 nm) / Zr getters, the pressure drop by the gettering for active gases, which were reported by main residual species in the FED panel, could be achieved from 9×10^{-5} Torr to 1×10^{-6} Torr or below except water vapor, on the contrary of results shown in Fig. 5. The poor sorption property of water vapor was due to its relatively low purity compared to other gases used in this experiment. The total absorbed quantity into the getter did not show a large difference between Ni(40 nm) / Zr and Pt(20 nm) / Zr getters, while the sorption kinetics of carbon monoxide and hydrogen were significantly increased at the same pressure conditions. This enhancement of sorption kinetics is mainly due to the species of surface catalytic layer. Ni and Pt have been widely used for catalysis of hydrogenation. However, Pt seemed to show the catalytic property in dissociation for other active gases such as carbon monoxide, carbon dioxide and oxygen in addition to hydrogen. Further investigation of this is now under progressing. From the results of above sorption properties, it could be known that Pt is more desirable as a catalyst and a protection layer in the fabrication of thin film getters for the FED.

IV. Conclusion

As a solution to the easy appliance of getters for FED, we developed the thin film getters employing the coating of new materials such as Ni or Pt on getter surface. Those can be used without any activation process and show the enhanced sorption characteristics, because the Ni and Pt have the catalytic property for hydrogenation and protect getter material from oxidation during handling process. However, in order to obtain their sufficient properties, those should be deposited over 20nm thickness. The sorption kinetics for hydrogen could be

enhanced by making the morphology of getters porous. Using the Zr(1 μm) thin film getters with the surface layer of Ni or Pt, the significant gettering for active gases could be achieved from 9×10^{-5} Torr to 1×10^{-6} Torr or below. However, the thin film getters with Pt surface layer showed better sorption kinetics than those with Ni layer.

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