Study ink-jet ink for surface electron emission materials applied in flat panel display technology

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Abstract
In this study, ink-jet technology is applied to the emitter fabrication for surface-conduction electron-emitter display (SED). The general emiiter material of SED, palladium oxide (PdO), is prepared by calcination the mixture of solvent and precursors of platinum chlorine and platinum nitrate. With controlling the precursors and solvents, the PdO is formed below 400℃ which is required for SED process.

1. Introduction
Surface-conduction Electron-emitter Display (SED), which function is similar to CRT, has high response speed and high resolution. The cathodes on the substrate emit electrons for exciting phosphors. The most difference between SED and CRT are emission sources.

The radiate mechanism of CRT is emitting electron beam by the heated filament to excite phosphors. However, the field emission technology used in SED makes every electron emit directly to each corresponding element on the screen. By this way, SED can keep not only the colorful properties of CRT which is much better than LCD, but also the advantages of flat plane and small weight and volume.

In this study, the ink-jet paste is prepared from metal precursors for ink-jet printing in making the field emission sources. The different reaction temperatures are controlled to form the proper emitter. To employ high emission efficiency material and low cost, as the gate, source and drain metals are an important and potential project.

This study focuses on the comparison of different precursors, calcination temperature and solvent to prepare field emitter. The optimum parameters for ink-jet procedure are decided according to several factors, including viscosity of ink-jet precursors, the composition and morphology of electrodes, the calcination temperatures, and electrode properties after calcination.

2. Experimental
Platinum chloride ($PdCl_2$) and platinum nitrate ($Pd(NO_3)_2$) are used as precursors to form the electrodes of platinum oxygen (PdO) in this study. Platinum chloride is bought from STREM CHEMICALS, USA. Platinum nitrate is obtained from Wako Pure Chemical Industries, Ltd., Japan with Wako 1st grade.

0.1 g $PdCl_2$ and $Pd(NO_3)_2$ powder is dissolved in 6 ml ethylene glycol, respectively. After ultrasonic vibration, the solution is dripped on the substrate and followed by calcination in air and oxygen.

In order to fit the proper viscosity of real ink-jet process and decrease the formation temperature of PdO electrodes, other different solvents such as glycerin, H_2O, and hydrogen peroxide are introduced to mix with ethylene glycol.

The thermo-gravimetry analyzer (TGA) is used to observe the decomposing temperatures of precursors in air and oxygen. The compositions of specimens are characterized and determined by energy-dispersive spectroscopy (EDS) of JEOL JSM-5600. Furthermore, the microstructures of specimens are observed by scanning electron microscope (SEM), JEOL JSM-6300.

3. Results and Discussion
3.1 TGA Analysis
Figure 1 is the TGA analysis of precursors with ethylene glycol after heating from 30 to 900 ℃ in air and oxygen. According to the results, it is found that $Pd(NO_3)_2$ has lower decomposing temperature (below 150 ℃) than $PdCl_2$ (above 500 ℃), and this means only $Pd(NO_3)_2$ is possible to form PdO electrodes at lower temperature.

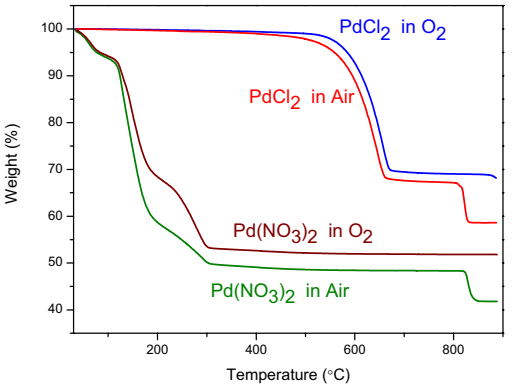


Figure 1 TGA results of precursors with ethylene glycol after heating from 30 to 900 ℃ in air and oxygen.

3.2 Electric properties

Figure 2 is the resistances of electrodes of two specimens after calcination from 100 to 600℃ in air and oxygen. PdO is a kind of metal oxygen, and its resistance is much higher than that of metal Pd. According to the results of electric properties, it indicates that the formation temperature of PdO for the specimen using $Pd(NO_3)_2$ precursor is blew 400 ℃. At the same time, the resistances of specimen using $PdCl_2$ precursor have no significant change even after calcination at 600 ℃.

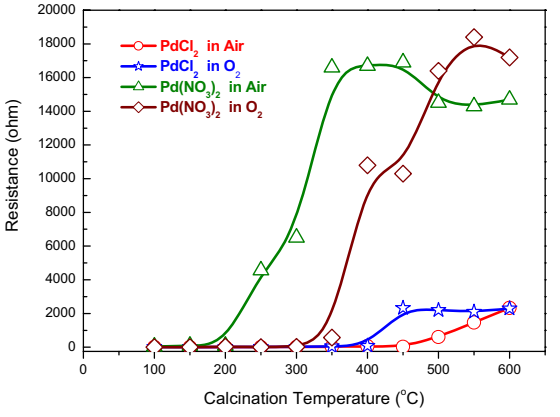


Figure 2 Resistances of electrodes for the specimens using different precursors after calcination from 100 to 600 ℃.

3.3 EDS Analysis

EDS analysis, shown in Figure 3, also has the same tendency toward resistances results. According to EDS results, the element oxygen in the specimens using $Pd(NO_3)_2$ precursors appear after heat treatment above 300 ℃. And this implies that oxide begins to form in the specimen using $Pd(NO_3)_2$ precursors between 300 and 400 ℃. However, the specimens using $PdCl_2$ precursor appear no oxide even after calcination at 600 ℃.

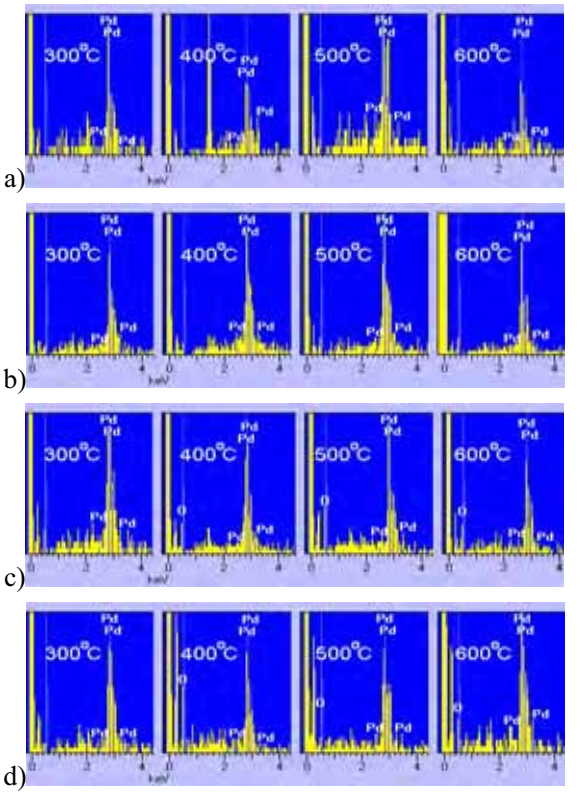
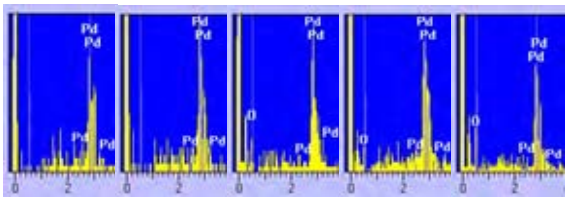


Figure 3 EDS results of specimens using $PdCl_2$ precursors after calcination in (a) air and (b) O_2, and using $Pd(NO_3)_2$ precursors after calcination in (c) air and (d) O_2.

Further, the specimens using $Pd(NO_3)_2$ precursors are heated in air from 350 to 390 ℃ for confirming the formation temperature of PdO, shown in Figure 4. According to these results, it is found that the specimens using $Pd(NO_3)_2$ precursor form PdO electrodes above 370 ℃.



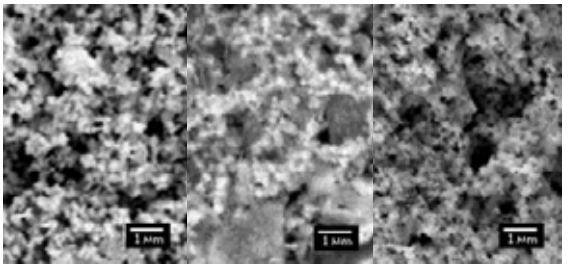
(a) (b) (c) (d) (e)

Figure 4 EDS results of electrodes using $Pd(NO_3)_2$ precursors after calcination at (a) 350, (b) 360, (c) 370, (d) 380 and (e) 390 ℃ in air.

3.4 SEM Analysis

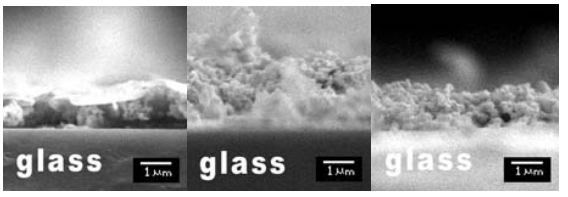
SEM results of the specimens using $Pd(NO_3)_2$ precursor mixed with ethylene glycol after

calcination at 370, 380 and 390 ℃ in air are showed in Figure 5 (top views) and Figure 6 (sectional views). The images show that the electrodes are the nanostructures consisting of necking nanoparticles with diameter of less than 100 nm after calcination in air. This kind of nanostructure is suitable to form the gap for the filed emission tips in the SED process.



(a) (b) (c)

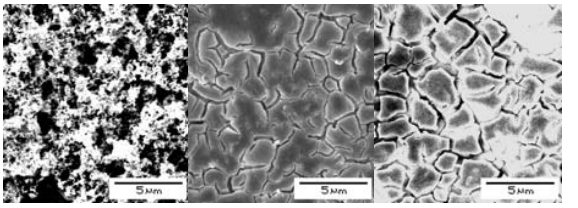
Figure 5 SEM results of the top views of specimens using $Pd(NO_3)_2$ precursor mixed with ethylene glycol after calcination at (a) 370, (b) 380 and (c) 390 ℃ in air.



(a) (b) (c)

Figure 6 SEM results of the sectional views of specimens using $Pd(NO_3)_2$ precursors mixed with ethylene glycol after calcination at (a) 370, (b) 380 and (c) 390 ℃ in air.

SEM images of the specimens using $Pd(NO_3)_2$ precursors mixed with different solvents after calcination at 370 ℃ in air are showed in Figure 7. The specimen mixed with ethylene glycol and glycerin solvents is consisting of nanoparticles which connect with each other, shown in Figure 7(a). However, there are many large cracks in the morphologies for the specimen mixed with H_2O and hydrogen peroxide after calcination in air, shown in Figures 7(b) and 7(c), respectively. These large cracks will break the flow of electrons during the SED operation. Therefore, glycerin can be used as the solvent to mix with ethylene glycol, and the ratios of these two solvents can be adjusted for the viscosity needed in inkjet printing process.



(a) (b) (c)

Figure 7 SEM images of specimens using $Pd(NO_3)_2$ precursors mixed with (a) glycerin and ethylene glycol, (b) H_2O, and (c) hydrogen peroxide after calcination at 370 ℃ in air.

4. Conclusion

The flat panel displays has trended in large size application. The epitaxy, lithography and etching issues have thus been widely concerned in uniformity. With the application of ink-jet technique, it is printed and coated the patterns on substrate through ink-jet head directly. The ink-jet materials can be prepared by mixing the metal precursors with proper solvent. In this study, $Pd(NO_3)_2$ precursors mixed with solvents, i.e. glycerin and ethylene glycol, can form the oxide electrode with nanostructures after calcination above 370℃ in air. Thus, this is prospect that ink-jet technique is applicable in preparing the insulator, semiconductor and conductor layers as future technique for display industry.

5. Acknowledgements

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6. References

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