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Nanogap formation by palladium hydrogenation for surface conduction electron emitters fabrication

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Nanometer-scale gaps in Pd strips are obtained by hydrogen absorption under high pressure treatment. The resulting lattice constant increase due to the Pd phase transformation after hydrogen uptake results in a large compressive stress on the thin Pd films. Under proper geometric arrangement of the Pd electrode within a surface conduction electron (SCE) emitter structure, a single nanogap per SCE device is obtained. A turn-on voltage of 41 V is observed for emitters with a 25 nm gap. © 2007 American Institute of Physics. [DOI: 10.1063/1.2728761]

Electrodes with nanometer separation have many potential applications, such as molecular electronics,^{1,2} biosensors,³ and vacuum microelectronics.⁴ However, most of the related nanogap studies are still in their infancy stages for practical applications because of the complexity and unreliability of nanogap fabrication and manipulation of nanosized constituents. One of the nanogap applications most possible to be realized in the very near future is surface conduction electron (SCE) emitters for flat panel displays, which has attracted much attention since the reports by Nomura *et al.*⁵⁻⁷ The nanogap in the SCE emitter was fabricated in palladium oxide electrodes prepared by ink-jet printing. To produce the nanogap, the PdO electrode was subject to a series of forming and activation processes. Although the SCE displays show many performance advantages over most contemporary flat panel displays, such as better brightness and low power consumption, the nanogap fabrication method is rather complicated and expensive. In this letter, we report a simple method to fabricate nanogaps in Pd thin film strips by high pressure hydrogen absorption treatment. When Pd is exposed to hydrogen gas, dissociatively adsorbed hydrogen atoms can quickly diffuse into the Pd lattice and occupy the interstitial site.^{8,9} The Pd-H system has two distinct phases, a hydrogen solution phase α and a hydride phase β . The two phases may singly exist in a pure form or coexist in the Pd-H system depending on the Pd:H atomic ratio and the absorption temperature. The β phase (4.025 Å) has a lattice constant larger than the α phase (3.894 Å) by 3.3%. The phase transformation from α phase to β phase is accompanied by a volume expansion of $\sim 12\%$, resulting in a large compressive stress in the Pd thin film. By properly designing the geometric structure of the Pd electrode in the SCE structure, we could concentrate the compressive stress induced by the phase transformation in a confined region and thereby produced a single nanogap in the SCE emitter.

The Pd nanogap SCE emitter was fabricated on a *p*-type (100) silicon wafer. Figure 1(a) schematically shows the cross section of the SCE structure. Nine nanogap emitters were connected in parallel with the comb-structured Pt electrodes, as shown in Fig. 1(b). The Si wafer was first ther-

mally oxidized to form a SiO₂ insulator layer of 150 nm thick, followed by photolithography process to define the Pt electrode pattern. A 5 nm thick Ti and a 10 nm thick Pt thin films were then sequentially deposited on the wafer by electron-beam evaporation deposition. After the photoresist lift-off by acetone forming the Pt/Ti electrode with a line-width of 30 μm , a second lift-off process was carried out to deposit Pd strip with one end overlapping the Pt/Ti electrode and the rest deposited on the SiO₂ insulator. The Pd strip was 30 nm thick, 3 μm wide, and 50 μm long. The Pd/Pt/Ti stacked structure on the SiO₂ layer was then placed in a stainless steel cell with a base pressure of 5×10^{-3} mbar for hydrogen absorption treatment. During the absorption treatment, the hydrogen pressure in the cell was kept around 2×10^4 mbars and the substrate temperature of 25–300 °C. After the hydrogen absorption, the cell was evacuated to 0.3 mbar and the sample was kept in the cell for 30 min at 330 °C for hydrogen removal. After the nanogap formation, lift-off lithography process was performed again to deposit a comb-structured Pt(50 nm)/Ti(5 nm) film stack on the gate side of the cracked Pd strip, and thus the preparation of the SCE emitter structure was completed.

Figure 2 shows the plane-view secondary electron microscope (SEM) images of the nanogap formed on three Pd electrode strips at different hydrogen absorption temperatures. Only one single nanogap was produced on each Pd electrode at the area immediately adjacent to the step edge of

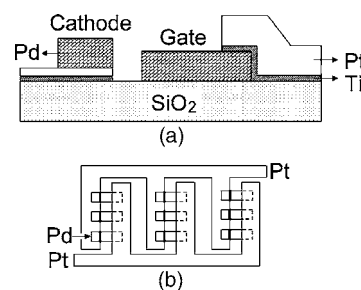


FIG. 1. (a) Schematic diagram of the cross section of the SCE emitter structure. (b) Nine SCE emitters are connected in parallel with the comb-structured Pt electrodes. The thick bar in each emitter denotes the nanogap formed on the Pd electrode.

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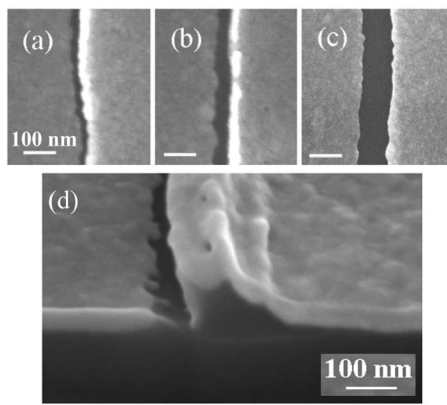


FIG. 2. SEM images of the nanogaps formed on the Pd strips in the SCE structure at different hydrogen adsorption temperatures: (a) 25 °C, (b) 200 °C, and (c) 300 °C. The scale bar indicates a length of 100 nm. (d) The side-view SEM image of the Pd nanogap of a 25 nm separation. The cross section of the nanogap was prepared by a focused ion beam.

the underlying Pt/Ti stacked layer. No crack was observed in other areas on the Pd thin film strip. The separation and edge roughness of the nanogap increased with the hydrogen absorption temperature. The nanogap formed at 25 °C [Fig. 2(a)] was ~ 25 nm wide, and was the smallest as compared with the other two nanogaps prepared separately at 200 and 300 °C, which had separations of ~ 50 and ~ 100 nm, respectively [Figs. 2(b) and 2(c)]. A focused ion beam (FIB) was used to prepare the cross section of Pd nanogaps, and the SEM image of the FIB-cut cross section of the nanogap of 25 nm separation is shown in Fig. 2(d). The breaking of the Pd electrode strip resulted in a drastic difference in the geometric shape of the two edges of the nanogap. The Pd electrode protruded along the gap edge on the side with the Pt/Ti underlayer and exhibited a jagged feature on the other side with a gradual film thinning toward the edge. The protrusion was several tens of nanometers higher than the gate surface. The observation clearly showed that a vigorous cracking process accompanied by extensive atom migration in the Pd electrode during the hydrogen treatment.

The rupture in the Pd strip was initiated by the stress developing at the step region as a result of volume expansion

due to the phase transformation from the α phase to the β phase of the hydrogenated Pd thin film. The stress induced by the phase transformation is much larger than that by thermal expansion. A value of compressive stress of ~ 5.0 GPa has been reported for hydrogenated Pd film on glass substrates.¹⁰ According to Hooke's law,

$$\sigma = \frac{E_{\text{Pd}}}{1 - \nu_{\text{Pd}}} \varepsilon, \quad (1)$$

the compressive stress due to a strain (ε) of 3.3% can be as large as 6.41 GPa, assuming Young's modulus (E_{Pd}) of 110 GPa and a Poisson ratio (ν_{Pd}) of 0.39.¹¹ Because the Pd strip was only 3 μm wide, the compressive stress developing in the Pd thin film during the phase transformation was likely to be partially relaxed in the lateral direction to reduce the resulting strain, and, therefore, little crack could be initiated on the strip. However, the step edge of the Pt/Ti underlayer created a discontinuity for the stress relaxation, and a large stress could accumulate within the region close to the step, leading to the rupture of the thin Pd strip and thus the formation of the nanogap. We have performed finite element analysis to study the hydrostatic stress distribution in the SCE structure after the phase transformation. We found that the region along the step edge had developed the largest stress. Figure 3 shows the stress distribution map of the cross section of the emitter structure subject to the hydrogen treatment at 25 °C. Parameters required for the simulation were film thickness, thermal expansion coefficient and elastic modulus, and Poisson ratio of the material constituents of the emitter structure. The mechanical property of the Pd-H system was assumed to be little dependent on the hydrogen concentration in the stress range of interest,¹² and thus elastic constants of metallic Pd were used for the simulation. It can be clearly seen that the stress induced by the volume expansion of the Pd thin film accumulated at the corner of the step bottom of the Pd layer and above the step edge of the Pt/Ti underlayer, as marked by the open circles. On the other hand, the top area near the step edge on the Pd layer was much less stressed, as marked by the square. Crack initiation in the Pd thin film in the step region due to the high stress concentration could result in the rupture of the Pd strip along the step

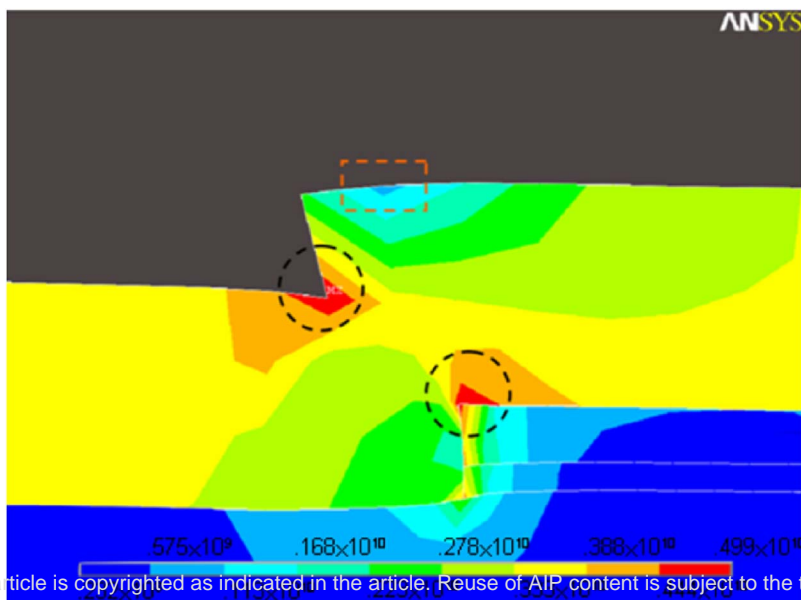


FIG. 3. (Color online) Hydrostatic stress distribution in the SCE emitter structure after hydrogenation treatment. The areas marked by circles are with the maximal stress and by square is the least stressed.

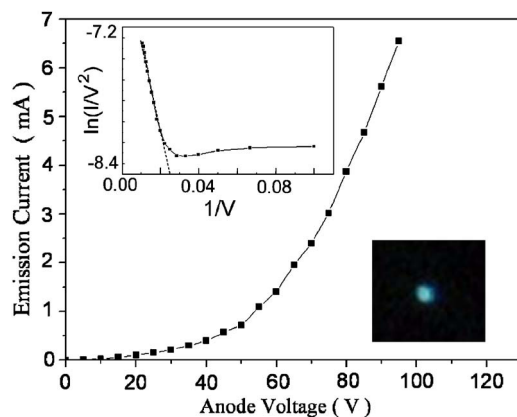


FIG. 4. (Color online) Conduction current between the cathode and the gate as a function of the gate bias. The correspondent FN plot is shown in the inset. The light spot shown on the lower right was produced on a phosphor plate of $500 \mu\text{m}$ apart from the SCE emitter array and biased by 2.5 kV with respect to the cathode.

edge via the process of stress relaxation through atomic diffusion driven by the stress gradient. During the breaking of the Pd strip, Pd atoms in the highly stressed region diffused toward the top area near the step edge, where was least stressed as compared to other area around the step, thereby a nanogap developed with the growth of a protrusion on the cathode side with the underlying Pt/Ti stacked layer.

The kinetics of developing the nanogap due to the stress gradient may be described by the stress-induced voiding model, which is considered as a process of void nucleation and growth.¹³ The void growth depends on many factors, such as stress, mechanical modulus, atom diffusivity, and temperature. Under the hydrogenation condition of a high absorption pressure, complete phase transformation from the α phase to the β phase must occur to all the three samples prepared at different absorption temperatures⁸ and, therefore, the three samples presumably had similar material properties. Thus the increase in the nanogap separation with the absorption temperature could be ascribed to that the void growth rate was enhanced at higher absorption temperatures, leading to the formation of a larger nanogap separation.

Electron conduction characteristics of the SCE emitters were studied by a Keithley 237 measurement system under a vacuum condition of 5.0×10^{-6} Torr. Figure 4 shows the conduction current (I) as a function of the bias voltage (V) between the cathode and the gate electrode for the nanogap of 25 nm separation. Also shown in the figure is the Fowler-Nordheim (FN) plot of the I - V curve. The linear relationship in the higher voltage regime indicated that the electron conduction followed the Fowler-Nordheim field emission mechanism. The turn-on voltage of the SCE emitter, which is defined as the voltage at which the emission current begins to exhibit linear characteristic in the FN plot, was about ~ 41 V. The nine SCE emitters produced a conduction current of $\sim 390 \mu\text{A}$ at the turn-on voltage. To illustrate the potential of the SCE emitters for display applications, the image of a light spot produced on a phosphor plate at a gate bias of 50 V, which was $500 \mu\text{m}$ apart from the Pd emitter

array and biased by 2.5 kV with respect to the cathode, is also shown in Fig. 4. The SCE emitter array occupying a total area of $160 \times 300 \mu\text{m}^2$ could produce a clear light spot of ~ 1 mm in diameter. It is worthwhile noting that electrons could actually emit toward the gate side from any part of the inclining sidewall of the protruding cathode, depending the bias voltage and the local separation between the emission area and the gate. The inclining feature of the protrusion may become very useful to protect emission areas from being damaged by impurity ions during field emission operation. One of the major obstacles to practical applications of field emission devices is that the lifetime of the field-emitter can be significantly degraded by ion bombardment and sputtering on the emitter surface under a high vacuum operation condition.¹⁴ The inclining sidewall of the cathode may function as a shield protecting electron-emitting areas from being struck by impurity ions, which are accelerated vertically in the high electric field between the cathode and the anode.

In summary, we have fabricated one single nanogap in the Pd strip electrode of a SCE structure by high pressure hydrogen treatment. Upon hydrogen absorption, phase transformation from the α phase to the β phase occurred to the Pd strip leading to volume expansion, inducing a large compressive stress on the step edge of the SCE structure. The high stress concentration along the step edge resulted in stress relaxation and film cracking, thereby forming the nanogap. The SCE emitter with a nanogap of 25 nm separation had a turn-on voltage of 41 V, and a total conduction current of $390 \mu\text{A}$ could be produced from nine SCE emitters.

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