Vacuum Dependency of Si, Co Slicide and Mo Silicide FEAs

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Abstract

In this paper, it is reported that the anode current changes at the constantly applied gate voltages and the current-voltage (I-V) characteristics of Si, Co silicide and Mo silicide field emitter arrays (FEAs) depending on vacuum level from a 10^{-9} torr to a 10^{-6} torr. The mechanism of the robustness of anode current degradation of Mo silicide FEAs under poor vacuum conditions can be explained by the model of tolerance for the oxygen adsorption and oxidation at the silicide surface. Also, we present the changes of emitting area and work function of the emitters according to vacuum level.

1. Introduction

The electron emission properties of field emitters are very sensitive to the interactions with various residual gases within the vacuum envelope. The FEAs operate at relatively low temperature and the tip surfaces have a relatively high sticking coefficient when compared to the hot filament thermionic cathode. Also, the presence of energetic gas species and ions near the emitter surface, which are formed by field emission, and their interactions with tip surface lead to the surface state and the work function changes of a field emitter, resulting in the change of electron emission characteristics [1].

It has been reported that the oxygen containing species such as O_2, CO_2, H_2O and CO in a vacuum environment mainly cause the degradation of the emission current of field emitters. Even if the emitter surfaces were clean at some initial time, a monolayer of contaminants will form in less than 1 hour at 10^{-9} torr and in 1 second at 10^{-6} torr. Most common contaminants give rise to increase work functions of field emitters [1]-[3]. Especially, because silicon has many dangling bond at the surface, native oxide is easily formed on the surface of silicon emitter.

Therefore, for the practical applications of field emitter arrays (FEAs), it is essential to investigate the vacuum dependency of emission characteristics. However, the studies on emission current change of silicide FEAs depending on vacuum level have not performed in any literature.

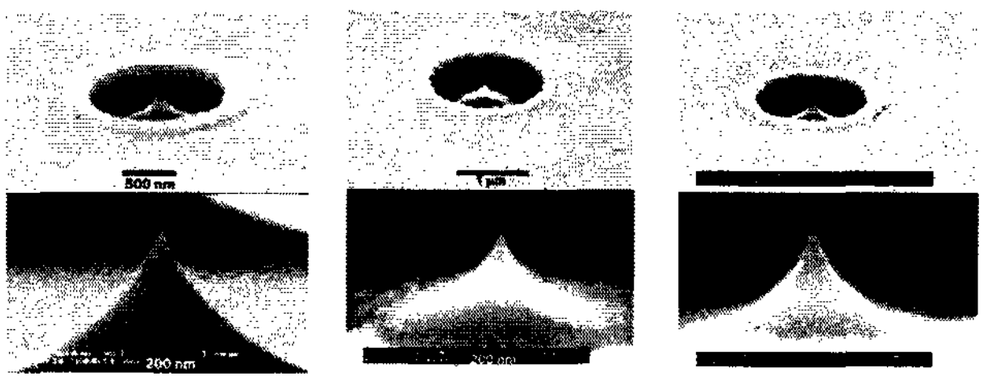
We recently reported on the fabrication and characterization of the Co silicide and Mo silicide FEAs [4], [5]. In this study, it is focused that the changes of the emission currents at the constantly applied gate voltages of the silicide FEAs depending on vacuum level from a 10^{-9} torr to a 10^{-6} torr. The mechanisms and explanatory models on the emission current degradation of the silicide FEAs, resulting from oxygen adsorption and oxidation, will be presented. To verify the validity of oxygen adsorption and oxidation models and analyze in detail anode current change depending on vacuum level, the changes of the field emission parameters such as emitting area and work function from I-V characteristics will be described.

2. Experimental

The 625 tip silicon FEAs with a gate opening of 1.4 μm were fabricated by dry etching and sharpening oxidation. Some of the silicon FEAs were splitted for metal deposition and followed by annealing for the silicide emitters. Coating Mo mono-layer (25 nm) and Ti/Co (15 nm/12 nm) bi-layers on silicon tips, and subsequent annealing by rapid thermal process (RTP) at 1000 °C and 800 °C, respectively, in inert gas (N_2) ambient produced Mo and Co silicides, respectively. After formation of the silicides, the unreacted metals and unwanted by-products were removed by wet etching [4], [5].

3. Results and discussion

Figure 1 shows the scanning electron microscopy (SEM) photographs of gated silicon, Mo silicide and Co silicide emitters. Using the SEM with 2 nm resolution, the measured tip radii of silicon, Mo silicide and Co silicide tips were 35 Å, 50 Å and 80 Å, respectively.



(a) (b) (c)

Fig. 1. SEM micrographs for the fabricated (a) silicon, (b) Mo silicide and (c) Co silicide emitters.

In order to observe the inertness and the stability of the silicide emitters to air molecules, the emitters were operated at ultra high vacuum (UHV) level of a 10^{-9} torr (period I) and the pressure was increased up to 10^{-6} torr by supplying room air (period II). Then the vacuum level was further increased to 10^{-9} torr (period III). During period II in Fig. 2, the emission currents of the silicide FEAs gradually decrease due to the adsorption of oxygen and formation of oxides on the tip surface with pressure increasing and then remain constant at the equilibrium state of reaction to air molecules, particularly of oxygen. On the other hand, the current of Si FEAs inconsistently changes. This is thought to be due to the formation of native oxide resulting in the reduction of anode current and the elimination of native oxide resulting in the increase in anode current, and/or the adsorption and desorption of unwanted gas. The anode current of Mo silicide FEAs was completely recovered back to the original value when the pressure was reduced to a 10^{-9} torr, whereas those of Si FEAs and Co silicide FEAs formed from Ti/Co were not recovered by merely reducing pressure. After baking for 20 minutes at 250 °C and under the pressure of a 10^{-9} torr, anode currents of Si and Co silicide FEAs were increased. However, the anode currents Co silicide FEAs did not completely return to their original values probably due to incompletely desorption of adsorbates and the elimination of oxides at the baking temperature, as shown at period III in Fig. 2.

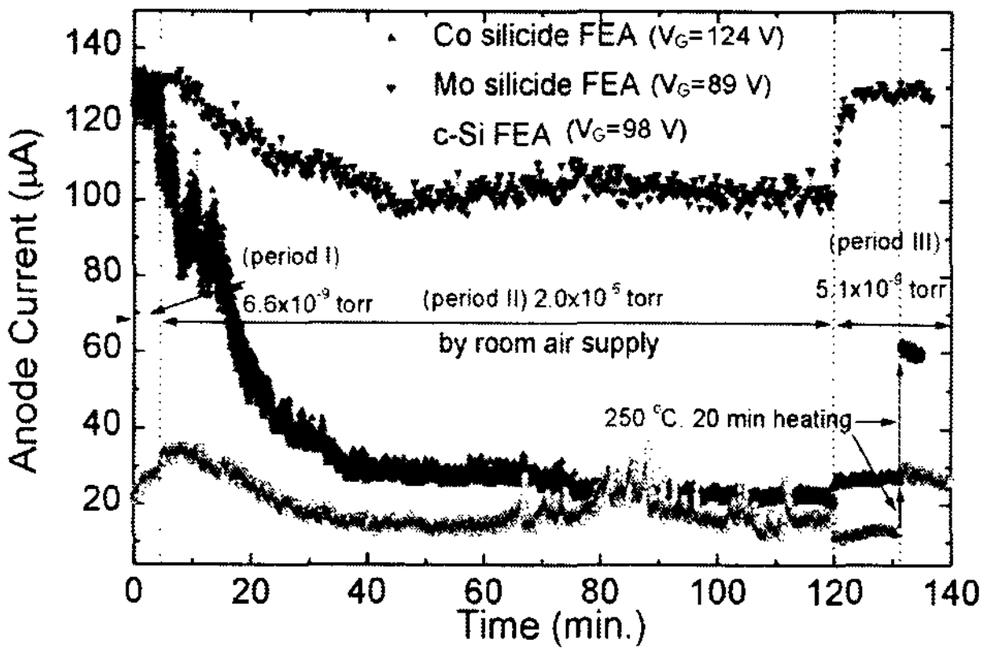


Fig. 2. Change of anode current depending on vacuum environment.

Macroscopic geometry changes in the emitter tips were not detected by inspection of SEM. Also, the fact that the emission characteristics returned to the initial values after vacuum level recovery suggests that the geometry changes are minimal, at least for the silicon and Mo silicide FEAs. Thus, the oxygen adsorption and oxide formations on the Mo and Co silicide tips under poor vacuum level of a 10^{-6} torr are main mechanism of the anode current degradations.

Figure 3 shows the schematic representation for the model of oxygen adsorption and oxidation on Co silicide FEAs. The oxygen atoms including neutral, meta-stable and ion species are formed by the field dissociation of oxygen bearing species and the impact of emitted electron. By the thermodynamics consideration, the heats of formation of Co oxides are higher than that of silicon oxide. So, Co silicide favors Si-O bond forming over Co-O bond forming. The oxygen including chemically active species reacts with Co silicide and the oxygen mainly bonds to the silicon, as shown in 1) of Fig. 3. The Co-Si bond is broken by the ion bombardment, the local heating of the tip surface and the reaction of the oxidant with the silicide. The silicon and cobalt at Co silicide surface become rich by the silicide dissociation. Consequently, the number of Si-O bond, SiO_2 formation and Co oxides formation are increased, as shown in 2) step of Fig. 3. For low temperature interactions, the phonon energies may not be high enough to break the Si-Si covalent bonds in silicon. Interstitial diffusion of cobalt atoms, which are main moving species in Co silicide, cause silicon bonds to weaken and eventually silicon atoms break away. The silicon atoms then diffuse into vacant metal sites in the silicide films. The fact that excess Si is generated for Co silicide suggests that the oxygen adsorption and oxidation reactions proceed quite readily. If the temperature of the silicon enclosed by Co silicide is as sufficiently high as exceed Si-Si covalent bond strength, the Si-Si bond is broken, as shown in 3) step of Fig. 3. Because silicon has very high self-diffusivity at high temperature, the broken silicon diffuses in Co silicide film, as shown in 4) step of Fig. 3. The transported silicon on the silicide surface is oxidized by reaction with oxygen and re-silicidized by reaction with free cobalt, as shown in 5) step

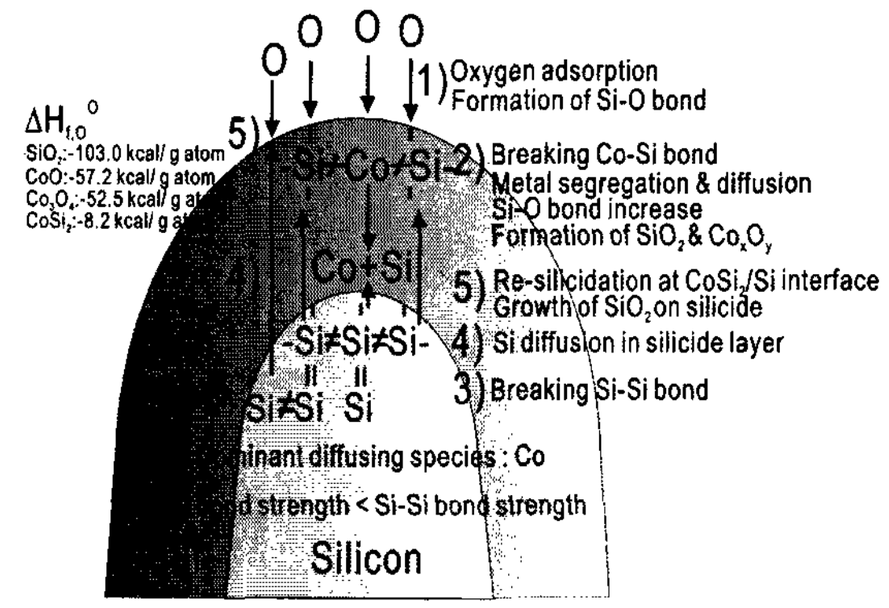


Fig. 3. Schematic representation for the model of oxygen adsorption and oxidation on Co silicide FEAs.

of Fig. 3. The silicon transport through the silicide is much faster than the transport of oxidant through the oxide. The liberated cobalt diffuses through the silicide to the silicide/Si interface to reform the silicide. Because the cobalt is the dominant diffusion species, the re-silicidation reactions occur at the interface between Si and Co silicide [6]-[8].

Figure 4 shows the schematic representation for the model of oxygen adsorption and oxidation on Mo silicide FEAs. By the thermodynamics consideration, the heats of formation of Mo oxides are higher than that of silicon oxide. So, Mo silicide favors Si-O bond forming over Mo-O bond forming. The oxygen including chemically active species reacts with Co silicide and the oxygen bonds to the silicon, as shown in 1) of Fig. 4. Because the Mo-Si bond strength is higher than Co-Si bond strength, it is more difficult to break a Mo-Si bond than a Co-Si bond. The liberated Si and Mo come from silicide dissociation are bond to oxygen, resulting in SiO_2 and Mo oxides formations, as shown in 2) step of Fig. 4. Since MoO_3 has the lowest heat of formation among Mo oxides, Mo oxide is mainly composed of MoO_3. MoO_3 is volatile species but Co_xO_y are non-volatile species. Even if the same number of metal-silicon bond is broken, the oxide formations on Mo silicide less than those on Co silicide owing to the sublimation of volatile MoO_3. The work functions of Mo and Co are about 4.5 eV and 5.0 eV, respectively. When the metals segregate in their silicide films, the transient fluctuation and emission characteristics of Mo silicide FEAs are better than those of Co silicide FEAs owing to the low work function of Mo. If the temperature of the silicon enclosed by Mo silicide is sufficiently high, the Si-Si bond is broken, as shown in 3) step of Fig. 4. Because silicon has very high self-diffusivity at high temperature, the broken silicon diffuses in Mo silicide film, as shown in 4) step of Fig. 4. Actually, in the case of Mo silicide, the required temperature for the Si-Si covalent bond breaking is more than 600 °C. However, this temperature is much higher than the temperature of the moderately operating tip. When the Si emitter with the tip radius of 35 Å emits 10 μA per tip, the array with 625 tips corresponds to 6250 μA, the tip temperature is about 600 °C. Therefore, Si-Si bond breaking is hard to happen in the moderately operating Mo silicide emitter. The transported silicon on the silicide surface is oxidized by reaction with oxygen and re-silicidized by reaction with liberal molybdenum, as shown in 5) step of Fig. 4. The silicon transport through the silicide is much faster than the transport of oxidant through the oxide. The liberated Si diffuses through the silicide to reform the silicide. Because the Si is the dominant moving species, the re-silicidation reactions occur at the surface of Mo silicide. With the progress of oxidation process, the mixtures of the oxides and Mo silicide exist on the original Mo silicide film, but the only oxides exist on the initial Co silicide film [6]-[8].

In order to analyze in detail the anode current change depending on vacuum level in Fig. 2, and investigate the validity of oxygen adsorption and oxidation model, the I-V measurements were also performed at the following several operation conditions; Before the measurement of anode current change under UHV (before period I), after device operation about 2 hours under 10^{-6} torr (before period II), after vacuum level recovering to UHV and after testing chamber heating under UHV (after period III), as shown in Fig. 5. From the F-N curves, we have estimated the relative changes in the work function and emitting area as a function of air pressure, assuming that the tip shape and radius remain unchanged. In order to obtain good values of linear fit with less than 1 % error for slopes of the F-N curves, the data of F-N curves of Si, Co silicide and Mo silicide FEAs were fitted in the relatively high gate voltage

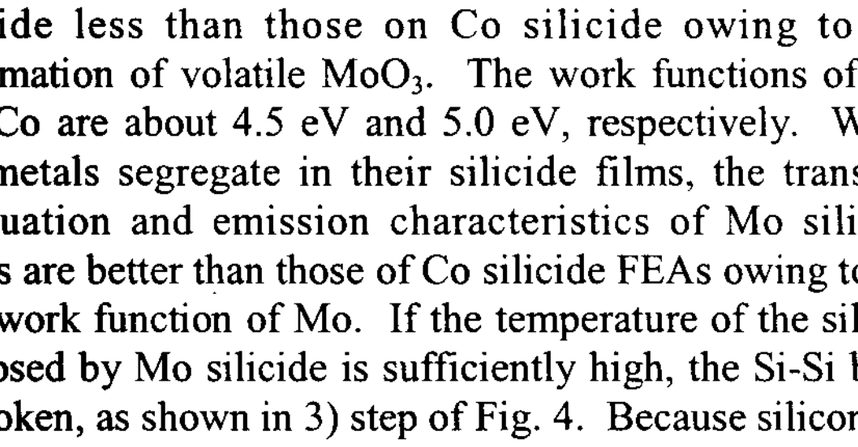


Fig. 4. Schematic representation for the model of oxygen adsorption and oxidation on Mo silicide FEAs.

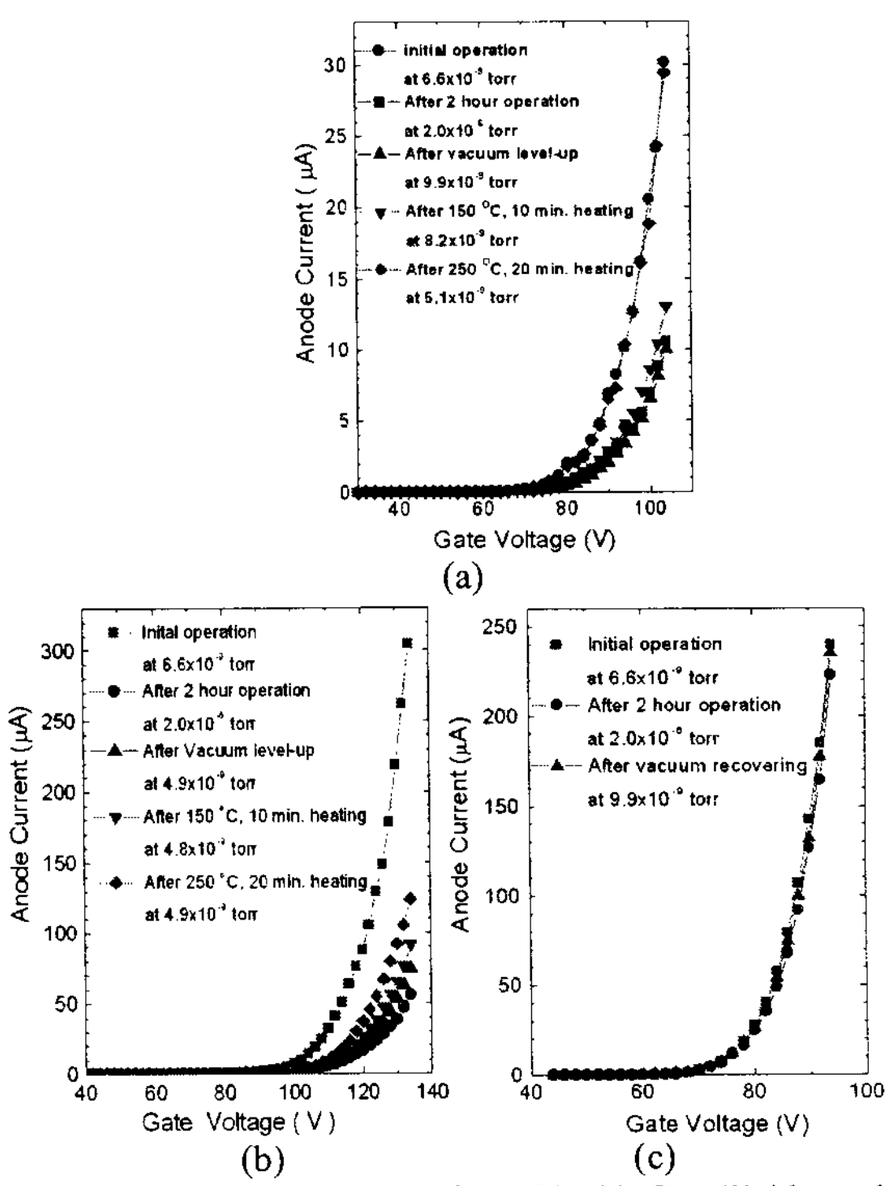


Fig. 5. I-V characteristics of (a) Si, (b) Co silicide and (c) Mo silicide FEAs with 625 tips under several operation conditions.

regime including the gate voltage of 98 V, 124 V and 89 V, the constantly applied voltages at the anode current measurement in Fig. 2, respectively.

The emitting area (α) and work function (ϕ) can be numerically calculated by the following equation. The equation can be derived by F-N plot and F-N equation [3]-[5].

$$\alpha_{F-N} = \frac{10^{C}\phi}{1.4\times10^{-6}\beta^{2}}\exp(-\frac{9.89}{\sqrt{\phi}}) = \frac{10^{C}S^{2}}{1.121\times10^{9}\phi^{5/4}}\exp(-\frac{9.89}{\sqrt{\phi}})$$

$$\left(\frac{\phi_2}{\phi_1}\right) \cong \left(\frac{S_2}{S_1}\right)^{\frac{2}{3}}\left(\frac{r_1}{r_2}\right)^{\frac{4}{9}}$$

where C, S and r correspond to the intercept on I/V_g^2-axis and the absolute value of slope of the Fowler-Nordheim plot, and tip radius, respectively.

After 2 hour operation of Si and Co silicide and Mo silicide FEAs under 2.0×10^{-6} torr, the effective work functions are slightly changed about +1.4 %, +0.9 % and -0.6 % and the emitting areas are remarkably reduced about 56 %, 78 % and 24 %, respectively, compared with those of initial operation under 6.6×10^{-9} torr due to the oxygen adsorption and the formations of silicon and metal oxides on the tip surface under 2.0×10^{-6} torr. Namely, the tip surfaces are locally covered by chemisorptions of oxygen, metal oxide and silicon oxide. As gate voltage increases, the cleaning effect of tip surface is easily apt to occur by desorption of contaminants, Joule heating and light ion bombardment. At a high gate voltage, the emitting atomic sites with low work function among the total emitting sites dominantly contribute to total emission current owing to high electron emission but the contribution of the emitting sites with high work function are nearly ignored due to low electron emission. So, the estimated work function at relatively high voltage regime is little changed. Conclusively, the small reduction in emitting area of Mo silicide FEAs under poor vacuum level shows Mo silicide FEAs is more tolerant to oxygen adsorption and oxidation at the tip surface than silicon and Co silicide FEAs. Also, this result supports the validity on the model of tolerance for the oxygen adsorption and oxidation of the Mo silicide FEAs.

Only by the vacuum level recovering to 9.9×10^{-9} torr, the emission current of Mo silicide FEAs is recovered to the value of initial operation. Instead, the emitting area is slightly decreased and the work function is little changed, compared with the results under 2.0×10^{-6} torr, due to the further exposure time of poor vacuum environments and the cleaning effect of dominant emission sites, respectively. After the vacuum levels is recovering to a 10^{-9} torr and the heating of test chamber, the emission currents and emitting areas of Si and Co silicide FEAs are not recovered to the values of initial operation due to incomplete desorption of adsorbate and elimination of oxides. But the emission currents and emitting areas are increased Si and Co silicide FEAs, in comparison with the operation results under 2.0×10^{-6} torr.

4. Conclusions

The vacuum dependencies of emission currents of Si, Co silicide and Mo silicide FEAs were investigated and compared, in the vacuum levels from a 10^{-9} torr to a 10^{-6} torr.

After 2 hour operation of Mo and Co silicide FEAs under 2.0×10^{-6} torr, the anode current reduction of the FEAs are about 11 % and 82 %, respectively, in comparison with the value of initial operation under a 10^{-9} torr. On the other hand, the current of Si FEAs inconsistently changes. The anode current of Mo silicide FEAs was completely recovered back to the original value when the pressure was recovered to a 10^{-9} torr, whereas those of Si FEAs and Co silicide FEAs formed from Ti/Co were not recovered by merely reducing pressure.

The mechanism of the robustness of anode current degradation of Mo silicide FEAs under poor vacuum conditions can be explained by the model of tolerance for the oxygen adsorption and oxidation at the silicide surface.

After 2 hour operation 2.0×10^{-6} torr, the emitting areas of silicon, Mo silicide and Co silicide FEAs are reduced about 56 %, 78 % and 24 %, in comparison with those of initial operation under 6.6×10^{-9} torr, respectively. Under poor vacuum condition, the small reduction in emitting area of Mo silicide FEAs supports the validity on the model of tolerance for the oxygen adsorption and oxidation at the Mo silicide surface.

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