Molybdenum and Cobalt Silicide Field Emitter Arrays

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Abstract

In order to improve both the level and the stability of electron emission, Mo and Co silicides were formed from Mo mono-layer and Ti/Co bi-layers on single crystal silicon field emitter arrays (FEAs), respectively. Using the slope of Fowler-Nordheim curve and tip radius measured from scanning electron microscopy (SEM), the effective work function of Mo and Co silicide FEAs were calculated to be 3.13 eV and 2.56 eV, respectively. Compared with silicon field emitters, Mo and Co silicide exhibited 10 and 34 times higher maximum emission current, 10 V and 46 V higher device failure voltage, and 6.1 and 4.8 times lower current fluctuation, respectively. Moreover, the emission currents of the silicide FEAs depending on vacuum level were almost the same in the range of $10^{9} \sim 10^{-6}$ torr. This result shows that silicide is robust in terms of anode current degradation due to the absorption of air molecules.

Keywords : Molybdenum silicide, cobalt silicide, field emitter arrays

1. Introduction

Metal silicides including Ti [1, 2], Co [2, 3], Nb [4], Mo [5, 6], Pd [7, 8], Cr [9] and Pt [10] were previously reported in various literatures to improve electron emission characteristics of Si FEAs. The advantages of silicide emitters have been mentioned as bwer effective work function, higher electrical conductivity, and better chemical and thermal stability than those of silicon emitters. Table 1 summarizes the results for various metal-silicide FEAs.

However, due to different emitter structure design and silicide formation process, the emitter materials including silicide phase and emitter structure including tip radius are not the same. Thus, the results presented in the literatures were not always consistent. Therefore, it is still important to study effective work function, and emission current characteristics for the silicide emitters, especially Mo and Co silicides. The properties of Si, Mo, Co, $MoSi_2$ and $CoSi_2$ are shown in Table 2.

To obtain the effective work functions, slopes of Fowler-Nordheim (F-N) curves are drawn and tip radii are measured by field emission scanning electron microscopy (FESEM). The emission current fluctuation and stability at a fixed gate bias and the emission current depending on vacuum level will be described.

2. Experiments

The 625 tip single crystal silicon(c-Si) FEAs with a gate opening of 1.4 μm were fabricated by dry etching and sharpening oxidation [11]. Some of the c-Si FEAs were split for metal deposition and followed by annealing for the formation of silicide on emitters. The Mo silicide was formed by coating with 25-nm thick Mo mono-layer on Si-tips and subsequent annealing in inert gas (N_2) ambient by rapid thermal processing (RTP) at 1000°C. Coating with Co mono-layer (25 nm), Co/Ti (18 nm/6 nm) and Ti/Co (15 nm/12 nm) bi-layers on Si-tips, and subsequent annealing by RTP at 800°C, 900°C and 800°C in inert gas (N_2) ambient produced Co

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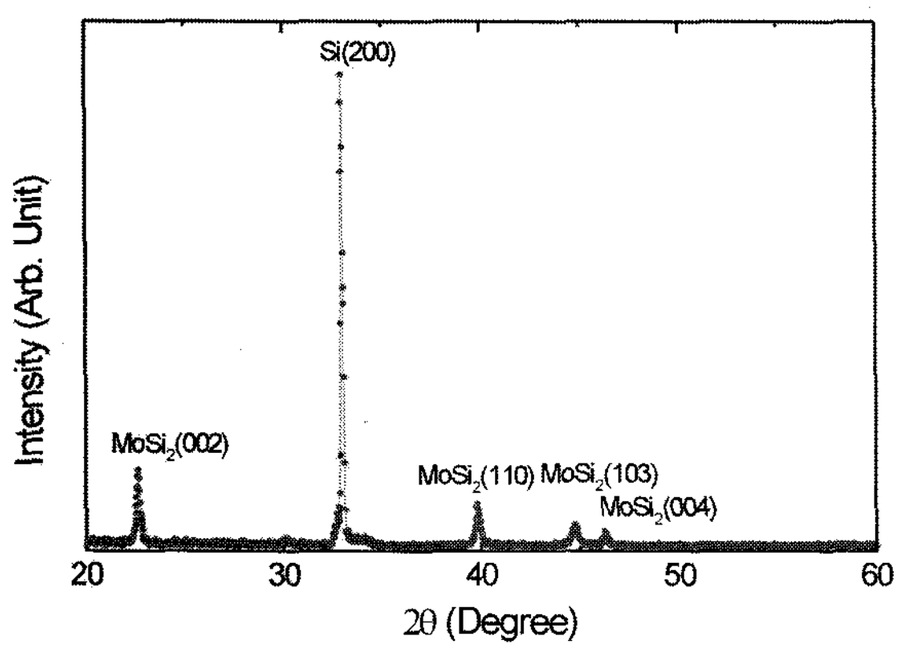
TABLE 1. Results of various metal-silicide FEAs

	Nb silicide (Nb_5Si_3, $NbSi_2$)	Mo silicide	Pt silicide (PtSi)	Pd silicide (Pd_2Si)	Cr silicide	Co silicide ($CoSi_2$)	Ti silicide ($TiSi_2$)
Num. of tips	3600	100	100	15000	16	10^5 tips/cm^2	10^5 tips/cm^2
Work function (eV)	3.1	3.1 (Si=4.05)	4.0 (Si=5.2)	8.31 5.0 (Si=4.8)	3.6 (Si=4.5)	2.31 (Si=4.34)	3.58 (Si=4.34)
Turn-on voltage (V)	47 (Si=64)	41 (Si=50)	62 (Si=84)	785	330 (Si=360)	180 (Si=220)	140 (Si=220)
Maximum current (μ A)	3.2	268 (Si=230)	350	27	3	0.4	0.35
Failure voltage (V)	60	129	100	1100	365	265	200
Emitter structure	Triode	Triode	Triode	Diode	Diode	Diode	Diode
Reference	[4]	[5]	[10]	[7], [8]	[9]	[2]	[2]

TABLE 2. Properies of Si, Mo, Co, $MoSi_2$ and $CoSi_2$

	Si	Mo	Co	$MoSi_2$	$CoSi_2$
Crystal structure	Diamond	Cubic	Cubic	Tetragonal	Cubic
Density (g/cm^3)	2.328	10.221	8.789	6.28	4.95
Melting point (^{o}C)	1420	2617	1495	2020	1326
Electrical resistivity (ρ at 300 K)	3.16×10^5 Ω-cm (Intrinsic) 1.0×10^{-3} Ω-cm ($\sim10^{20}$ cm^{-3})	5.78 μΩ-cm	7.6 μΩ-cm	22 ~ 100 μΩ-cm	10 ~ 18 μΩ-cm
ρ(293K) / ρ(4.2K)	–	1.26	1.91	1380	5
Lattice mismatch (%)	(a_{Si}=5.43095Å)	–	–	(a_{MoSi2}=b_{MoSi2}=3.203Å c_{MoSi2}=7.855Å)	-1.2 % (a_{CoSi2}=5.365Å)
Activation energy (eV)	–	–	–	3.2	2.8
Thermal expansion Coef. (ppm/^{o}C)	2.33	5	12	8.25	10.14
Microhardness (kg/mm^2)	–	191	–	735 ~ 1200	77 ~ 552
Young's modulus (Gpa)	170	320	210	430 ~ 440	160
Reference	[15]	[16] - [19]		[20]	



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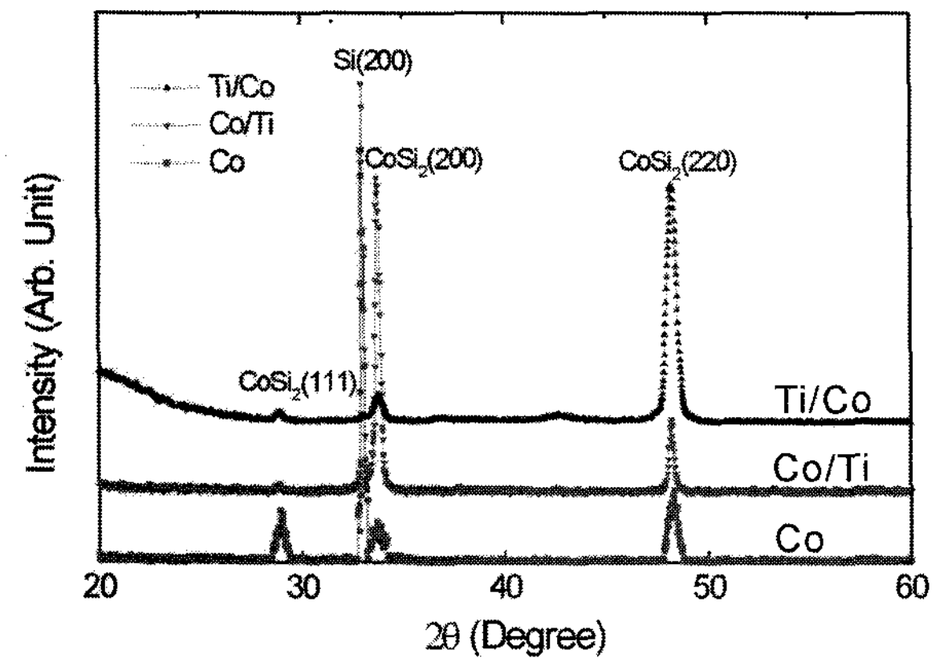


(b)

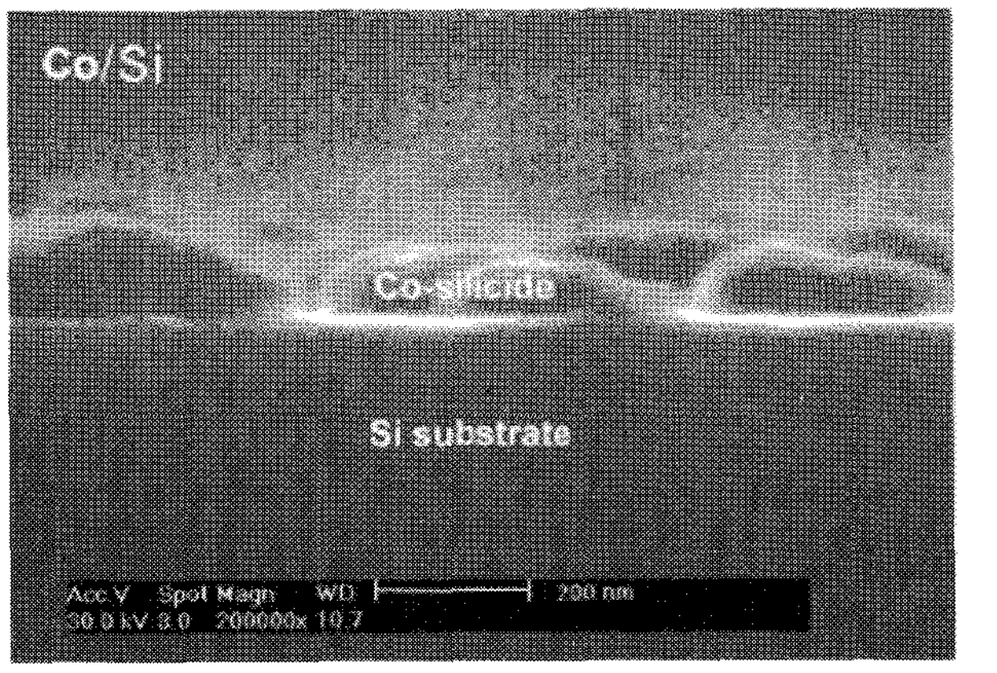
Fig. 1. X-ray diffraction spectra for the (a) Mo/Si and (b) Co/Si, Co/Ti/Si and Ti/Co/Si annealed in an N_2 ambient using RTA, after removal of the unreacted metals.

silicides. After the formation of the silicides, the unreacted metals and unwanted by-products were removed by wet etching.

3. Results and Discussion

In order to examine the phase identification of the metal-Si compounds, X-ray diffraction (XRD) measurement was performed. It was confirmed that Mo mono-layer and Co mono-layer, Co/Ti and Ti/Co bi-layers were completely transformed into $MoSi_2$ and $CoSi_2$ phases, respectively, as shown in Fig. 1.

SEM is used to analyze the Co silicide samples to check the surface morphology, thickness uniformity of Co silicide layers and $CoSi_2$/Si interfaces. As shown in Fig. 2, the sample formed from Ti/Co layer showsa very flat surface, uniform thickness of about 39 nm and



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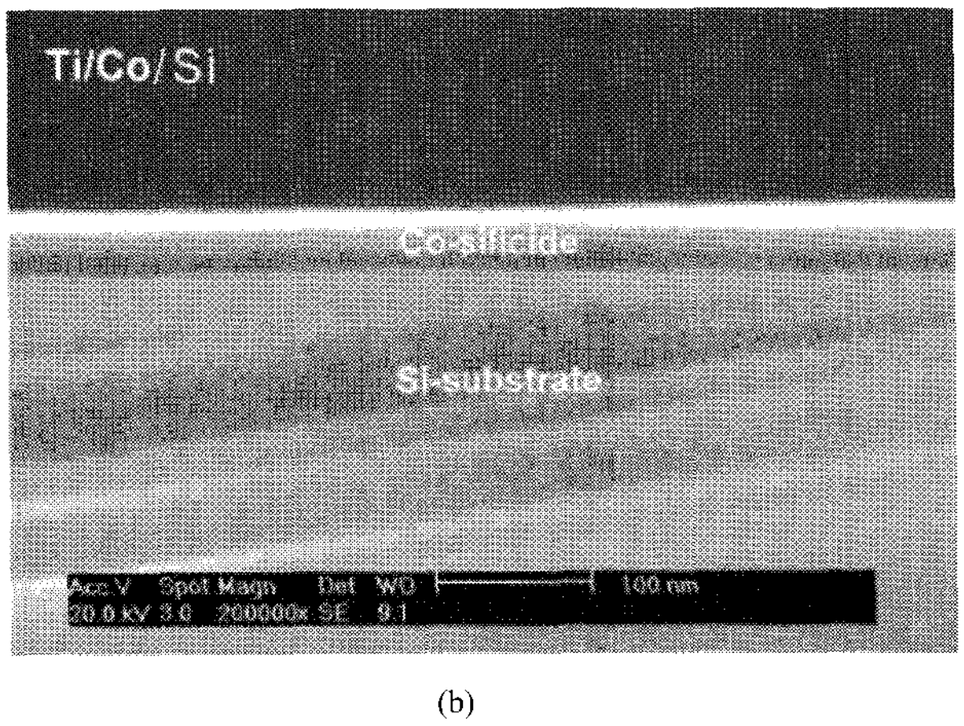

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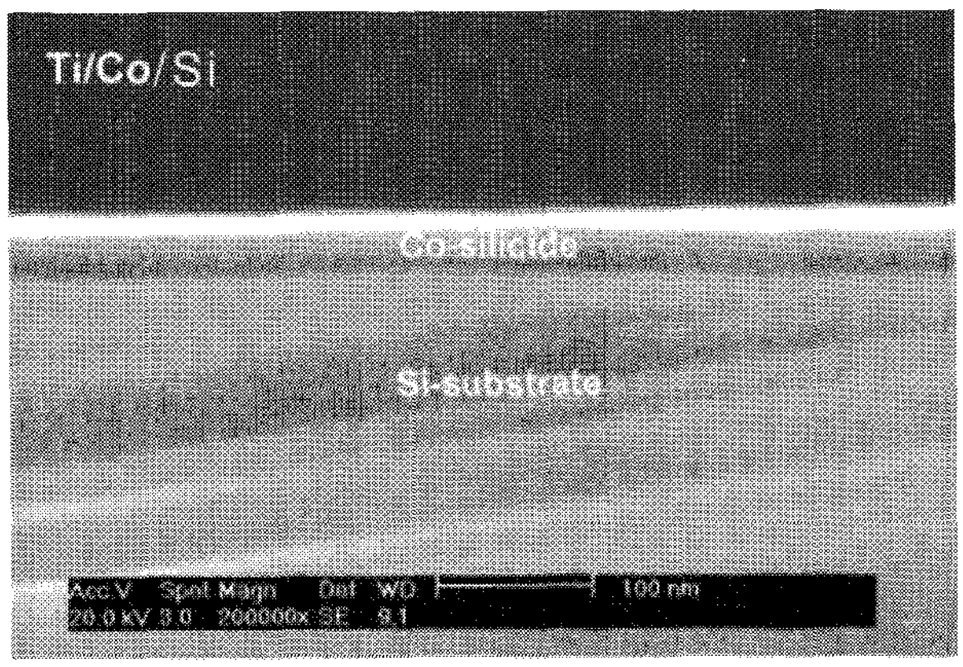
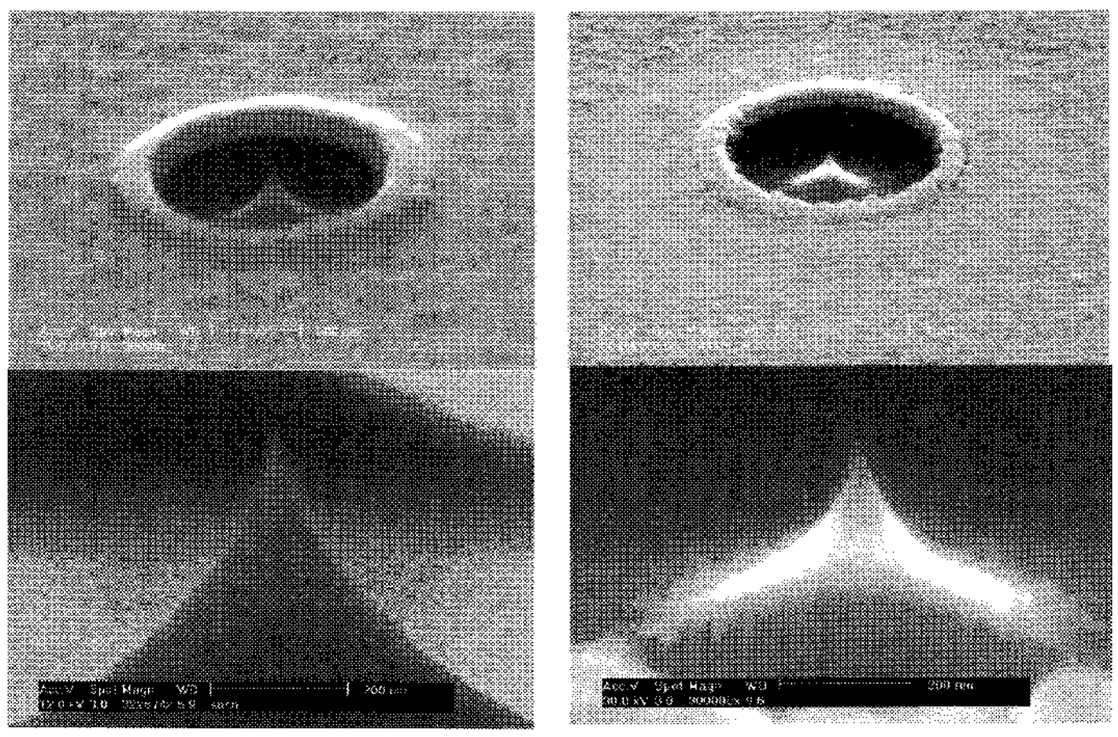


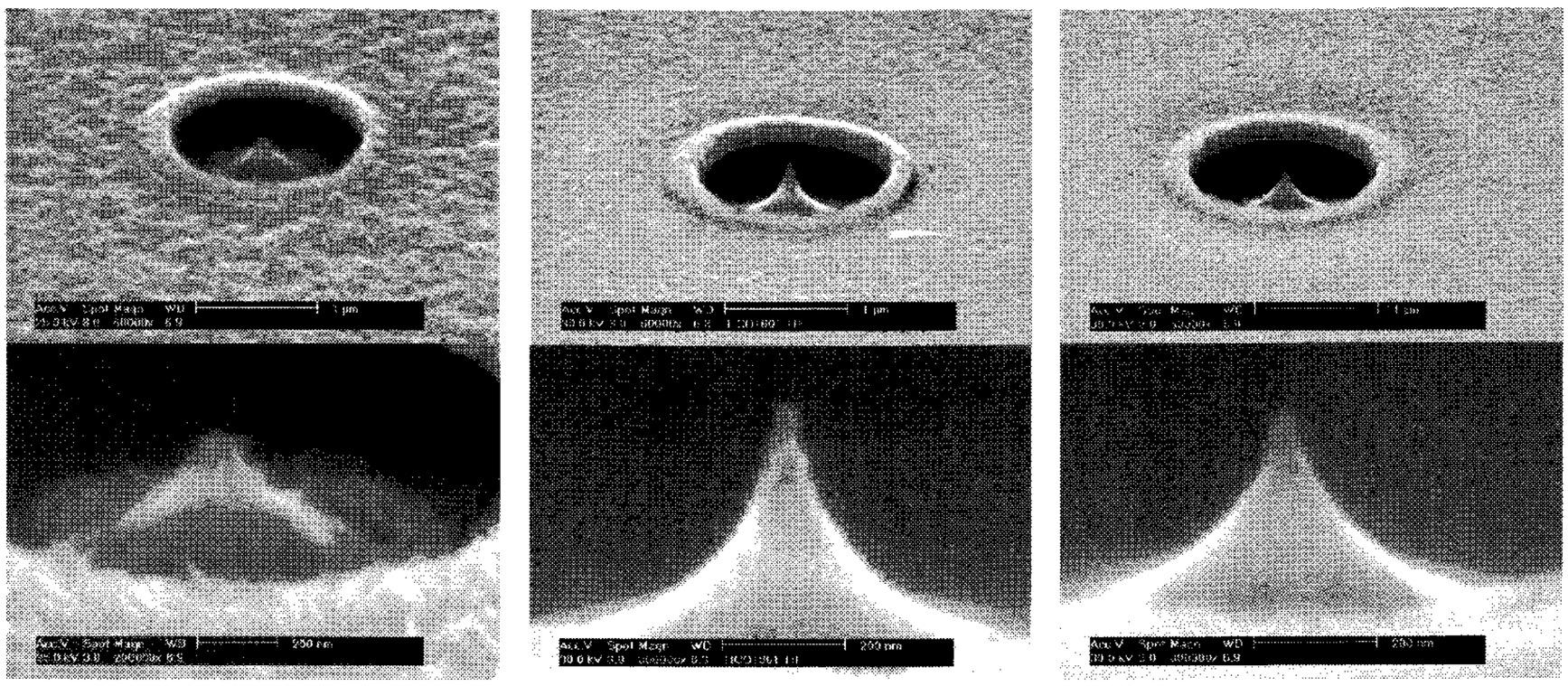
(c)

Fig. 2. SEM cross sectional views of Co-silicides formed by coating (a) Co(250 Å), (b) Co(180 Å)/Ti(60 Å), and (c) Ti(150 Å)/Co(120 Å) layers and annealing 800℃, 900℃, and 800℃, respectively.

smooth interface, because Ti prevents oxygen adsorption on the Co film during silicide formation [12]. However, the sample formed from Co mono-layer shows a rough surface and agglomeration due to adsorption of oxygen on the Co film. The quality of the silicide formed from Co/Ti layers in terms of surface roughness and thickness uniformity is in-between the two competitive samples,



(a) (b)



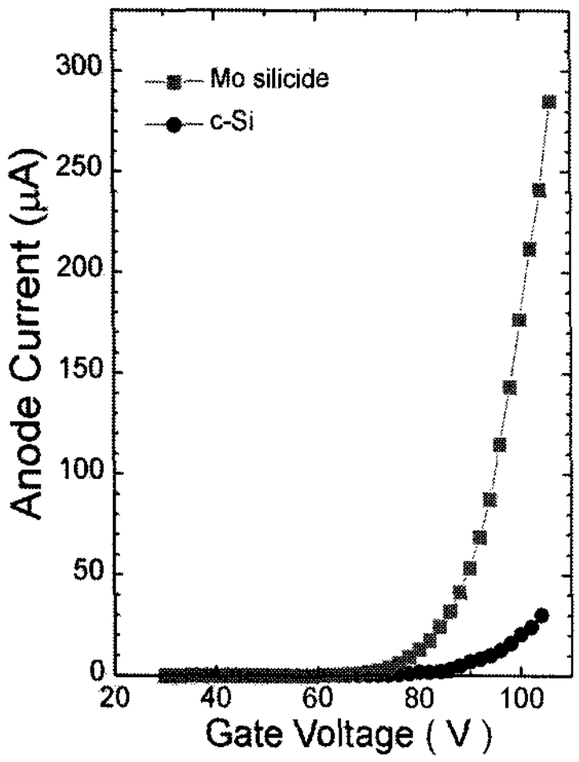
(c) (d) (e)

Fig. 3. SEM micrographs for the fabricated (a) c -Si emitter, (b) Mo silicide emitter and C o silicide emitter formed from (c) Co, (d) Co/Ti, and (e) Ti/Co. The tip apex of Mo and Co silicide tips became blunt compared with that of c -Si tip.

as shown in Fig. 2 ambient using RTA, after removal of the unreacted metals.

Fig. 3 shows SEM photographs of c-Si emitter, Mo silicide emitter and Co-silicide emitters formed on c-Si. Compared with c-Si emitter, the gate metal surface of Mo silicide emitter is somewhat made rough. The measured radii of silicon, Mo silicide, Co/Ti and Ti/Co tips were 35 Å, 50 Å, 115 Å and 80 Å with 10% error, respectively. The Mo silicide tip is much sharper than the Co silicide tips. The Ti/Co tip is the sharpest among the Co silicide emitters, although all the silicide tips are not as sharp as the initial c-Si emitter.

Field emission properties of the fabricated emitters were characterized in an ultra high vacuum chamber at a base pressure of 6.6×10^{-9} torr. Prior to the test, samples were heated for 10 hours at 250°C to remove residual gas including water vapor adsorbed on tip surfaces. The anode plate was 3 mm above the gate top and biased to +300 V. Figure 4 shows the I-V characteristics of c-Si and the silicide emitters with 625 tips. Fig. 4(a) shows that the anode currents at the gate voltage 100 V for the Mo silicide and the c-Si emitters are 176 μA and 21 μA, respectively. The Mo silicide emitters have lower turn-on voltage of about 8V than that of silicon emitters. As shown in Fig. 4 (b), Co silicide emitters formed from a Co mono-layer using RTA show about 46 V higher turn-on voltage than c-Si emitters and have high gate current which is about 38.5% of the anode current at the gate voltage of 150 V, due to tip blunting and rough surface, as shown in Fig. 3(c). In Fig. 4(c), the anode current from c-Si, Co/Ti and Ti/Co emitters are compared. The gate currents of silicon, Mo silicide, Co/Ti and Ti/Co



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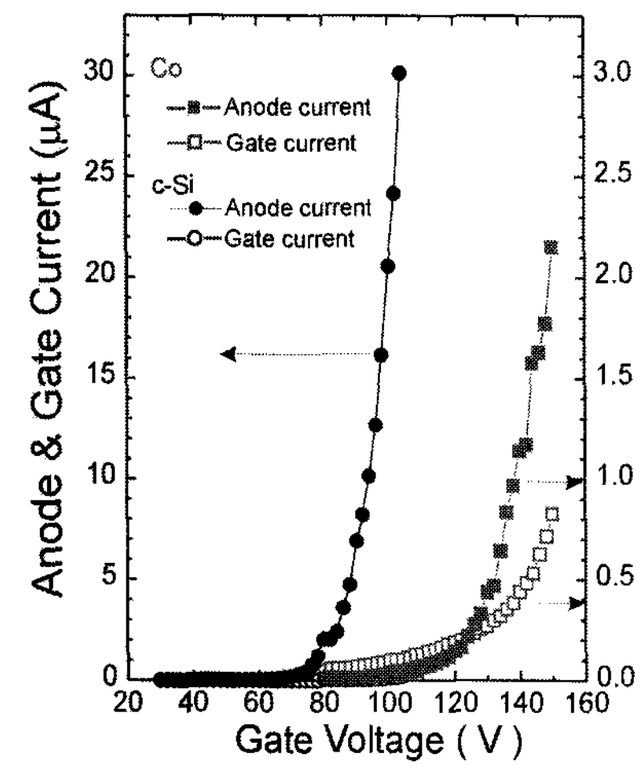

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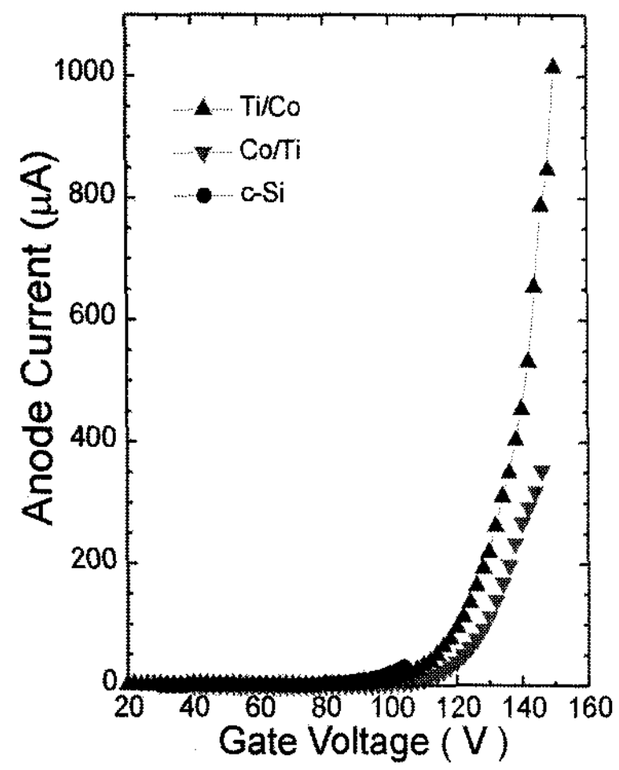
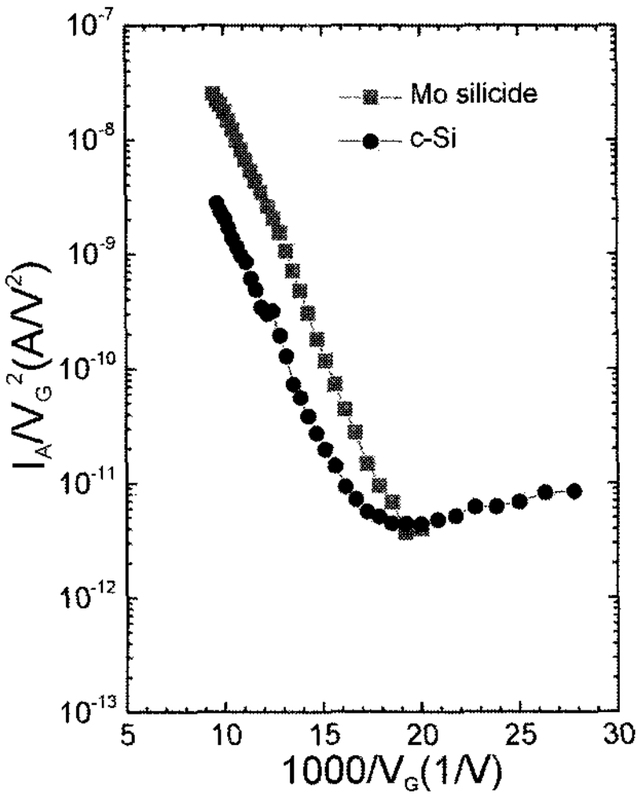


(c)

Fig. 4. I-V curves taken from c-Si FEAs, (a) Mo silicide FEAs and Co silicide FEAs formed from (b) Co mono-layer, (c) Co/Ti and Ti/Co bi-layers based on c-Si with 625 tips.



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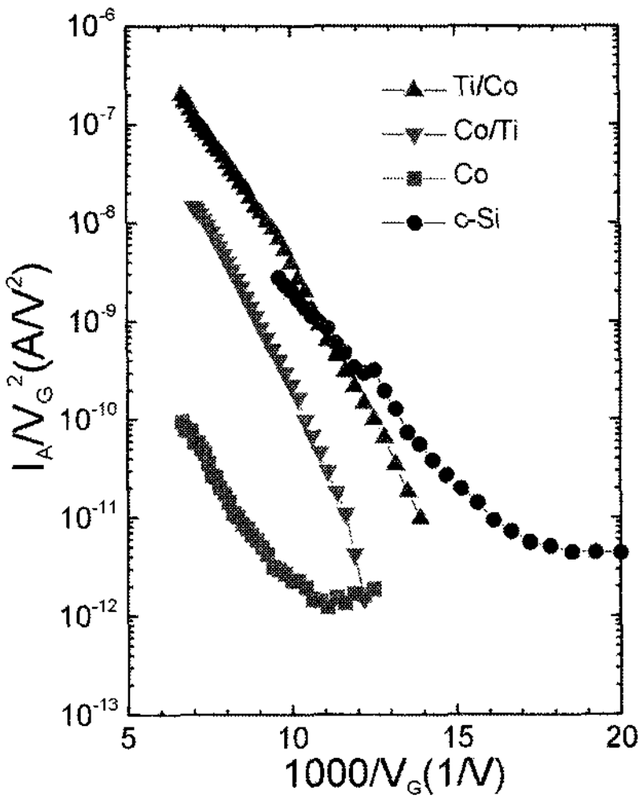

(b)

Fig. 5. F-N plots for (a) the Mo silicide and (b) the Co silicide FEAs The slopes of F-N curve of c-Si, Mo silicide, Co, Co/Ti and Ti/Co emitters are 0.4058 A/V, 0.3925 A/V, 0.4195 A/V, 0.6015 A/V, 0.6319 A/V and 0.4725 A/V, respectively. A/V stands for ampere/volt.

FEAs were less than 1.0%, 1.0%, 11.3% and 2.9% of the anode current, respectively. The required gate voltages of silicon, Mo silicide, Co/Ti and Ti/Co emitters to obtain anode current of 30 μA are 104 V, 86 V, 118 V and 109 V, respectively.

The device failure voltage is the voltage at which short occurs between gate metal and cathode tip. The device failure voltages of silicon, Mo silicide, Co/Ti and Ti/Co emitters were 106V, 116V, 148V and 152V, respectively. Our SEM study indicates that the emitter failure is due to arc between tip and gate electrode. Although the turn-on voltage of Co silicide formed from Ti/Co bi-layers is

higher than that of silicon emitters due to tip blunting (lower field conversion factor, β =1/5r), the silicide FEAs demonstrate the highest device failure voltage of 152 V and emission current of 1mA, as shown in Fig. 4(c), due to low electrical resistivity, high thermal conductivity, and smooth gate surface morphology [13].

Using Fowler-Nordheim(F-N) theory for the electron emission, the work function(ϕ) can be written as the following equation [13, 14].

$$\phi = \left(\frac{b\beta}{0.95B}\right)^{2/3} = \left(\frac{S}{0.95B \times \log e \times 5r}\right)^{2/3} \quad (1)$$

Where B is 6.87×10^7, β is the field conversion factor, r is the tip radius and S is the slope of F-N curve.

From the slope of Fowler-Nordheim plots in Fig. 5 and the tip radii measured from SEM photographs in Fig. 3, the effective work functions of c-Si, Mo silicide and Co/Ti and Ti/Co emitters are about 4.06 eV, 3.13 eV, 2.46 eV and 2.56 eV, respectively, which are similar to the previously reported results [2, 5].

The emission current variations of the Mo silicide FEAs normalized with average anode current at a fixed gate bias during 12 minutes ranged from–7.1% to +8.1%. In the case of Co silicide FEAs formed from Co, Co/Ti and Ti/Co, the variations ranged from –13.2% ~ +15.8%, –16.9% ~ +17.2% and –8.9% to +10.3%, respectively. The variation of silicon FEAs ranged from –37.1% to +55.3%, as shown in Fig. 6. The notable reduction of emission current variation in the silicide FEAs suggests that the silicide emitters are less influenced by gas adsorption and desorption and/or the destruction of sharp emission site than silicon emitters.

For the practical applications of field emitter arrays, it is essential to investigate the vacuum dependence of emission characteristics, because field emission properties depend sensitively on the work function change of the emitter surface by gas absorption [13]. Figure 7 shows experimental results on the change of the emission current depending on the vacuum level. The emission current of the c-Si FEAs decreases in the range of 10^{-9} ~ 10^{-6} torr. However, the currents of Mo silicide and Co silicide formed from Ti/Co are almost identical over the same range. This result shows that silicide is robust in terms of anode current degradation due to the absorption of air molecules.

In order to observe the inertness of the silicide emitters to air molecules, the emitters were operated at

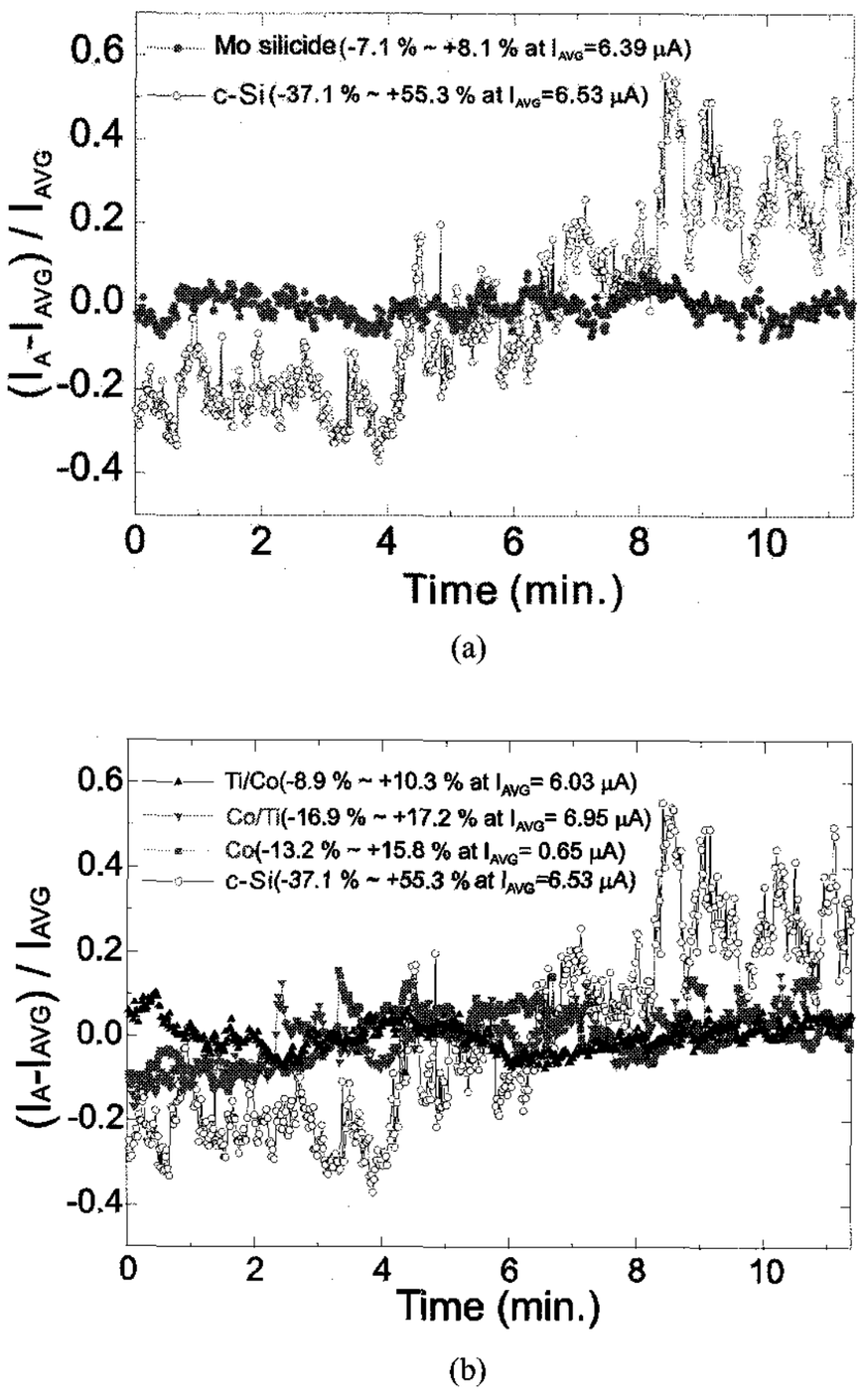

Fig. 6. The emission current variations of the c-Si and the silicide FEAs. The variation is defined as $(I_A-I_{AVG})/I_{AVG}$ at constant applied voltages, where I_{AVG} is the average anode current during the measurement.

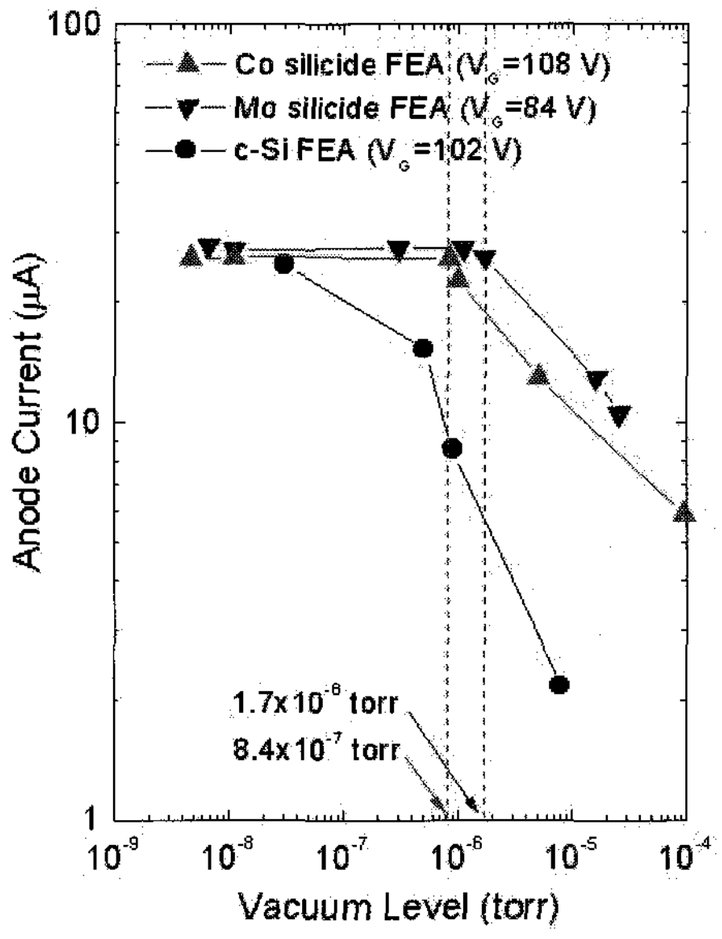

Fig. 7. Anode currents of Si, Mo silicide and Co silicide formed from Ti/Co FEAs with 625 tips depending on the vacuum level.

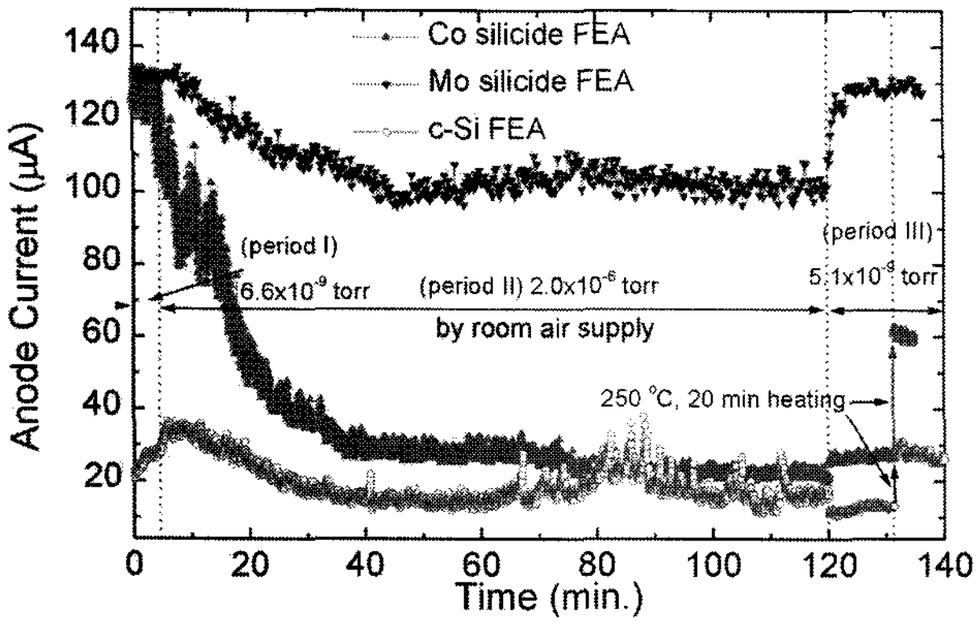

Fig. 8. Change of anode current depending upon vacuum environment.

high vacuum level of 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. 8, the emission current of the silicide FEAs gradually decreases and then remains constant. On the other hand, the current of c-Si FEAs inconsistently changes. This is thought to be due to the formation and deformation of native oxide, and/or the absorption 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 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 10^{-9} torr, anode currents of Si and Co silicide FEAs were increased. However, the anode currents of Si and Co silicide FEAs did not completely return to their original values probably due to incompletely desorption of air molecules at the baking temperature and/or tip surface modification during device operation, as shown at period III in Fig.8.

4. Conclusions

The Mo silicide FEAs can be obtained by depositing Mo mono-layer on c-Si tip and its annealing. Co silicides were formed from Co, Co/Ti and Ti/Co layers on c-Si FEAs. Uniform and smooth Co silicide layers can be obtained by depositing Co first and then Ti on silicon tips, followed by rapid annealing. Compared with c-Si field emitters, the silicide FEAs exhibited higher emission current, higher failure voltage, less emission fluctuation and better stability to vacuum environments. The better emission characteristics of the silicide emitters can be explained in terms of their lower effective work function, their lower electrical resistivity and their better surface inertness than those of the silicon emitters.

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