Silicon field emission arrays coated with a $CoSi_2$ layer grown by reactive chemical vapor deposition

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Abstract

We prepared Si emitters coated with a MOCVD $CoSi_2$ layer to improve the emission properties. The $CoSi_2$ layer was grown on Si field emitters *in situ* by reactive chemical-vapor deposition of cyclopentadienyl dicarbonyl cobalt at 600 ~ 650 °C. The $CoSi_2$ coated field emitters showed enhanced emission properties of current-voltage characteristics, which were due to the increase of emitting area from Fowler-Nordheim plot. And the emission current fluctuation decreased due to the chemically stable surface properties of $CoSi_2$.

Introduction

In vacuum microelectronic devices one of the ultimate goals is to develop an electron source of high efficient field emitter arrays. The low turn-on voltage and stable emission current are important factors for the application to the electron sources in the emissive flat panel displays (FPDs). Various materials such as molybdenum[1], silicon[2] and diamond[3] have been studied for a field emitter tip. Especially, silicon based emitters have been intensively studied by many researchers[4] due to the extensive knowledge about the process compatibility with integrated circuits (ICs). However, silicon emitters have problems such as relatively poor electrical and thermal conductivity and thin oxide layer that grows on the surface[5]. To solve the problems in the Si emitter tip, therefore, surface modifications such as metal coating[6], diamondlike carbon film coating[7], and silicide coating[8,9] have been performed. Metal silicide field emitters have been reported to have significant enhancement of emission current and stability[10,11]. But generally, the formation of metal silicide structure on silicon emitter has two steps such as metal deposition and conversion to silicide by thermal annealing at high temperature. In some case, capping layer on metal is required to prevent the agglomeration of silicide during thermal annealing.

In this study we present a new method to grow a $CoSi_2$ layer *in situ* on silicon emitters at 600 ~ 650°C from cobalt metallorganic source by reactive chemical vapor deposition (CVD). CVD commonly offers advantage such as a uniform conformal deposition over a large area and no substrate damage. We compared the emission characteristics of $CoSi_2$ coated field emitters and silicon emitters in the view of turn-on voltage, emission current, and emission current fluctuation.

Emitter Fabrication

A boron-doped p-type (100) silicon wafer with a resistivity of 5 ~ 20 Ω·cm was used as a substrate. LPCVD oxide films of about 4000Å were patterned for an etch-mask with a contact aligner, which results in a disc of 3μm in diameter. The silicon was etched using SF_6 gas by inductively coupled plasma (ICP) and the tips were sharpened by wet oxidation. Figure 1 shows the scanning electron micrograph of silicon emitters fabricated. Silicon emitters were coated with $CoSi_2$ by reactive MOCVD. Among the cobalt metallorganic sources, cyclopentadienyl dicarbonyl cobalt, $Co(\eta^5\text{-}C_5H_5)(CO)_2$, was used. The Co film was deposited from $Co(\eta^5\text{-}C_5H_5)(CO)_2$ at 110 mTorr with 10sccm H_2 carrier gas at the substrate temperature range from 500 to 650°C and $CoSi_2$ layer formed on silicon emitters *in situ*. The deposition time was 15min and thickness of $CoSi_2$ layer was 300-350Å. The resistivity of $CoSi_2$ layer was about 17.3 μΩ·cm. The crystal structure and composition of the film were investigated using x-ray diffraction (XRD) and Auger electron spectroscopy (AES), respectively. Field-emission measurements were carried out at a pressure of $2\text{-}3\times10^{-7}$ Torr by a diode-type arrangement. Anode plate, highly polished stainless steel for I-V measurements were separated from the cathode by 50μm thick insulating spacer films. The I-V curves were measured by ramping the bias voltage up and down, typically, in 20V steps.

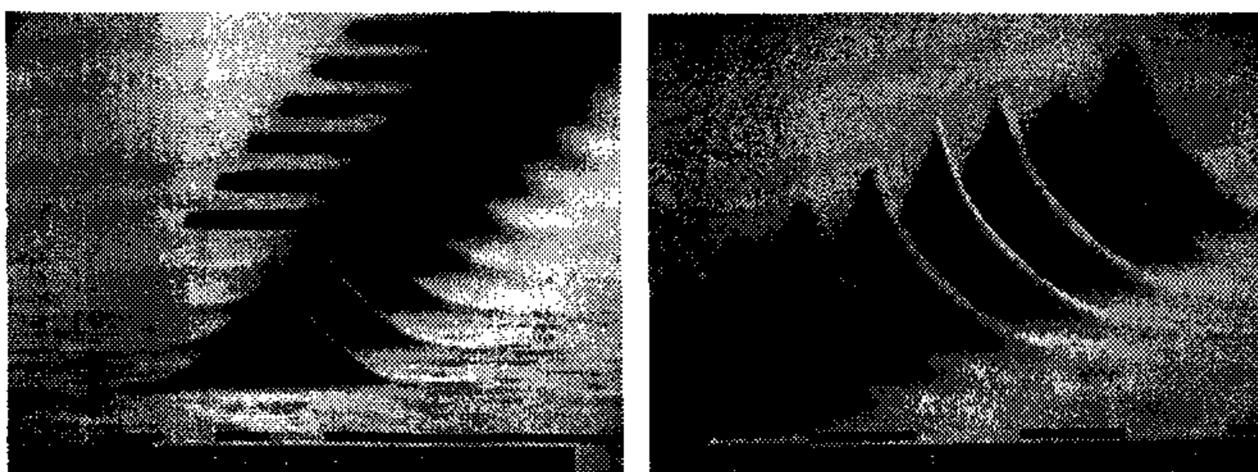

Figure 1. (Left) Scanning electron microscope (SEM) micrograph for a Si post array. (Right) The apex radius of the Si tip after sharpening oxidation followed by 6:1 BOE solution is observed to be ~ 30nm.

Results and Discussion

Figure 2 shows XRD patterns of the samples as deposited at 550, 600, and 650°C for 10min on (100) Si substrate, not on Si tips, from the $Co(\eta^5\text{-}C_5H_5)(CO)_2$ precursor. Above 600°C, only $CoSi_2(200)$ and Si(200) peaks exist without peaks such as (111) and (220). $CoSi_2$ phase with (100) preferred orientation can be formed by CVD of the metallorganic source without the phase transformation from the Co-rich phases such as Co_2Si and CoSi at high temperature.

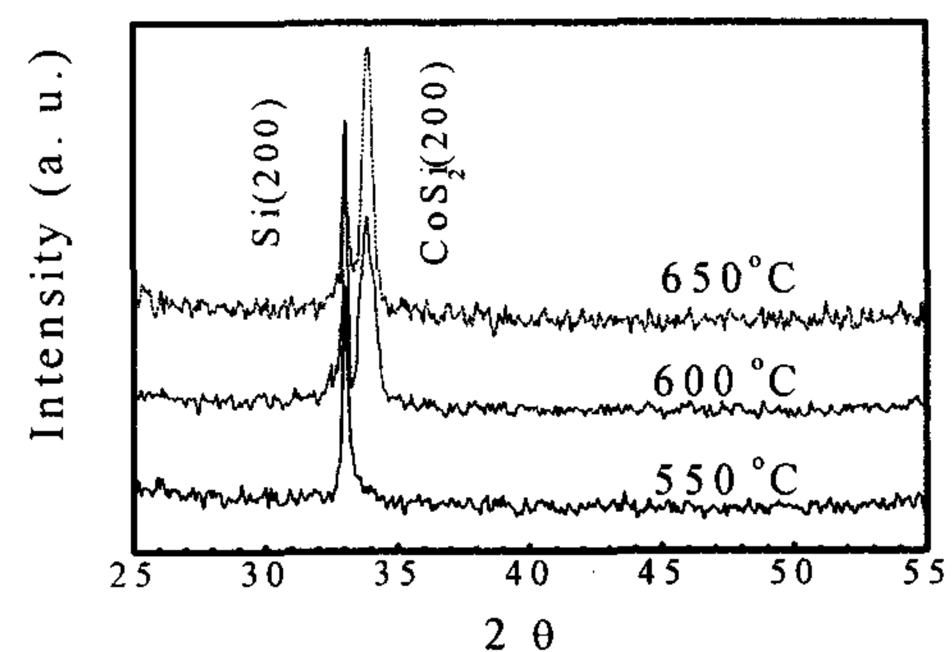

Figure 2. XRD patterns of the samples as deposited at 550, 600, and 650°C for 10min from $Co(\eta^5\text{-}C_5H_5)(CO)_2$ precursor.

Figure 3 shows the I-V characteristics in liner scale and Fowler-Nordheim (FN) plots for the Si FEAs before and after $CoSi_2$ deposition at 650 °C. The decrease of turn-on voltage and enhancement in emission current were observed after $CoSi_2$ coating.

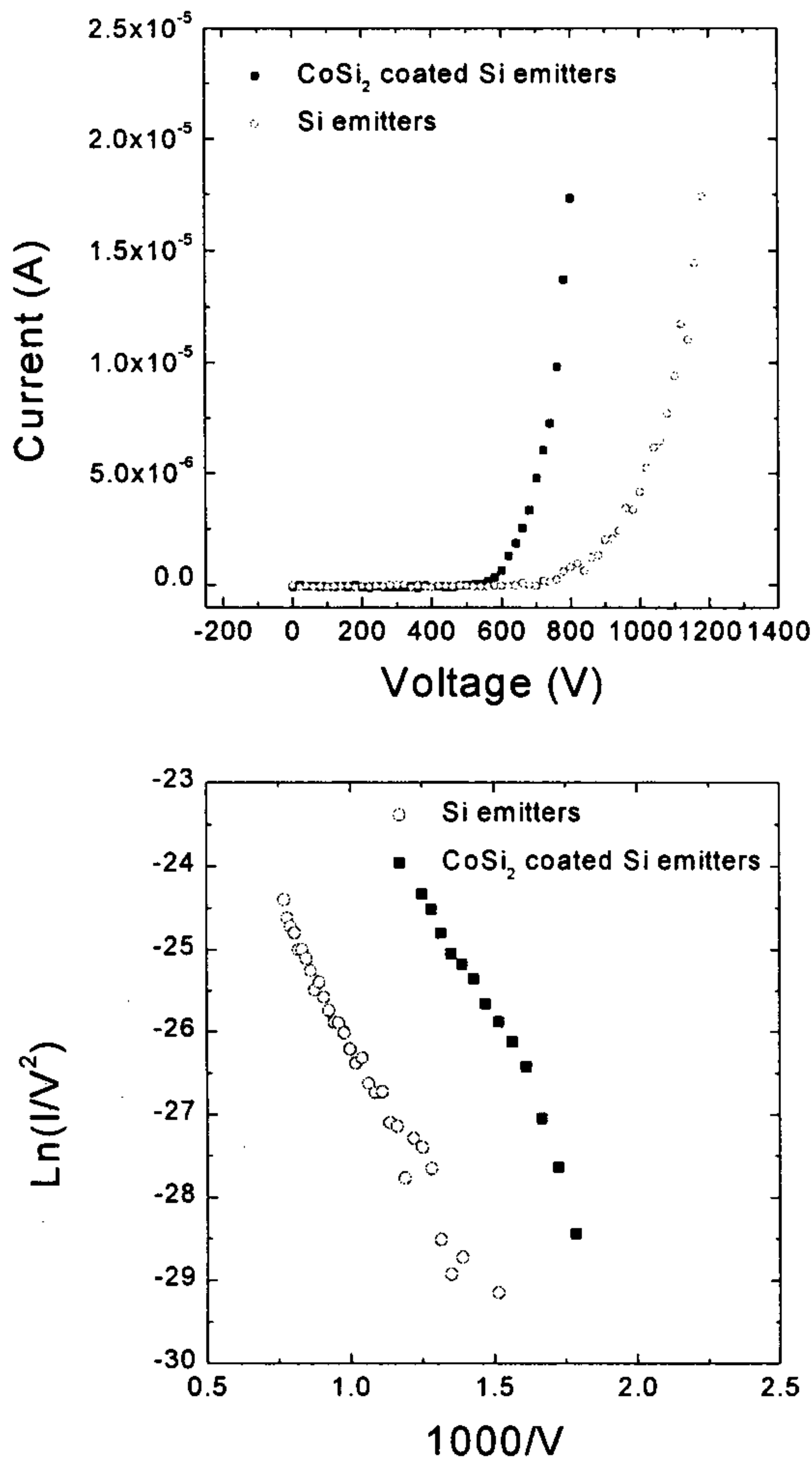

Figure 3. I-V and FN plots for 1000 Si FEAs before and after $CoSi_2$ coating

The emission current increased by a factor of 10. Therefore the average emission current per $CoSi_2$ coated emitters was about 18nA at the 800V. From the y-axis intersect of FN plot the emitting area of $CoSi_2$ coated emitters increased but the slope of the FN plots was not much changed. Assuming the geometrical factor of both FEA's is the same, the effective work function of $CoSi_2$ coated emitters may be almost the same as that of silicon emitters. Therefore, it is seen that the enhanced electron emission is largely due to the increase of emitting area by $CoSi_2$ formation, which has low resistivity compared with silicon[11].

Figure 4 shows the emission current fluctuation of the Si field emitters and the $CoSi_2$ coated field emitters. Constant DC voltages, 1000V to Si FEA and 800V to $CoSi_2$ coated FEA, were applied respectively. The current fluctuations were presented as anode current normalized with average emission current. The standard deviation decreased from 0.48 to 0.41 after $CoSi_2$ coating. This might be attributed to the chemical stability of $CoSi_2$ coated field emitters than that of Si field emitters[10,11].

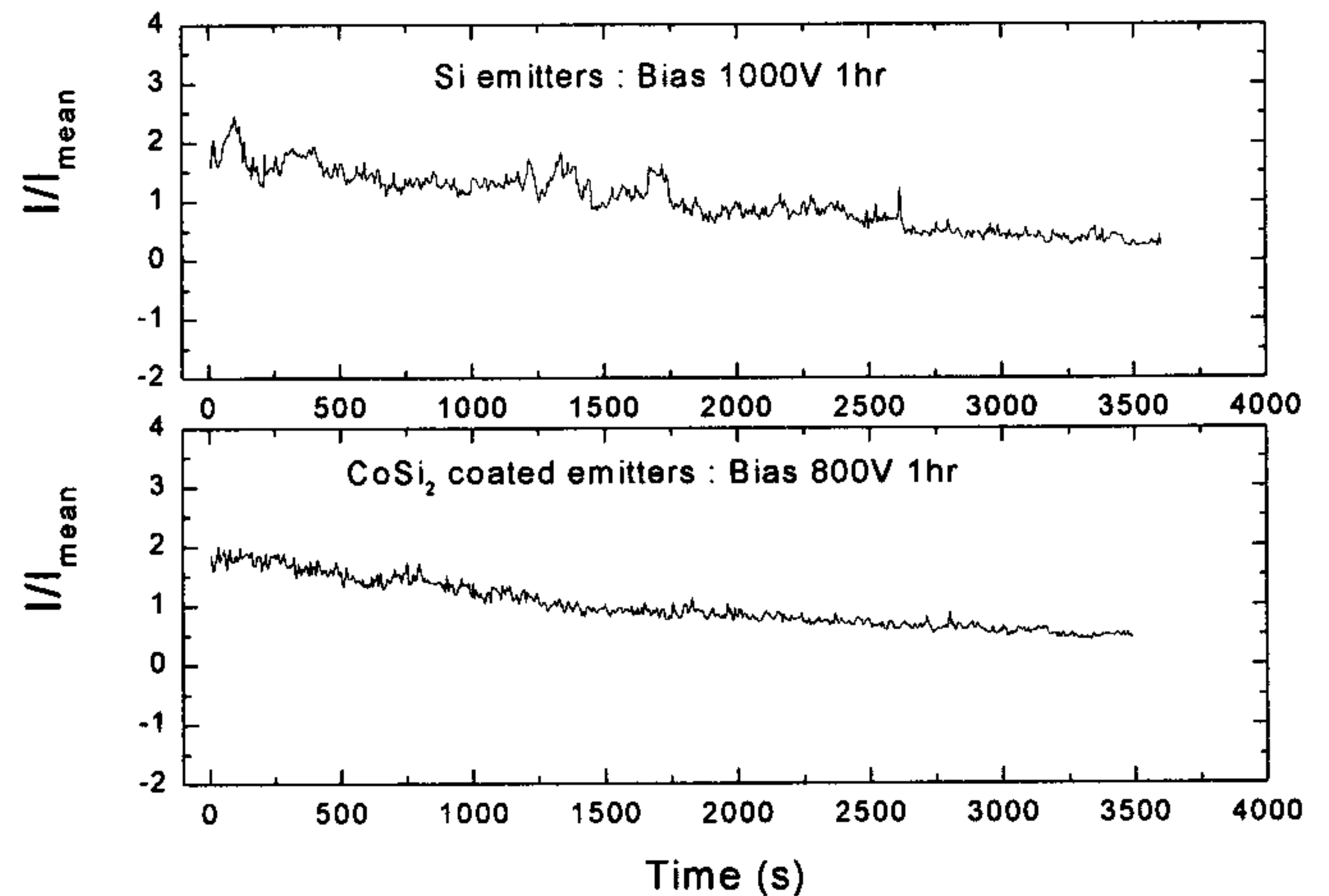

Figure 4. Emission Current normalized by mean current (I_{mean}), indicating emission current fluctuation before and after $CoSi_2$ coating.

Conclusion

We deposited an *in situ* $CoSi_2$ layer on silicon emitters at 600 ~ 650°C with cobalt metallorganic source, cyclopentadienyl decarbonyl cobalt, by reactive CVD. And we observed the emission characteristics of $CoSi_2$ coated field emitters improved. The enhanced emission properties were due to the increase of emitting area by the formation of $CoSi_2$ on silicon emitters from Fowler-Nordheim plot. It might be due to the low resistivity of $CoSi_2$ compared with that of silicon. And emission current fluctuation decreased due to the chemically stable surface properties of $CoSi_2$. A further study of emission current degradation with time is under investigation.

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