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Growth and Field Emission Characteristics of Pillar-like Carbon Nanotubes Using Co-Ti /Al Co-deposited Catalysts at Low Temperature

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In this essay, the pillar-like CNT field emission arrays synthesis with co-deposited catalysts at low temperature (550℃) was proposed. Pillar-like CNT has been successfully synthesized by thermal CVD system. The current density of this proposed pillar like CNTs was as high as 1272 μA/cm^2 at 6 V/μm and the turn-on field was 3.6 V/μm. Additionally, the reliability was more stable as lower than 7% degradation of initial current density.

Introduction

Due to the development of semiconductor processes and the investigations of nano-scale materials, the technologies and device structures of vacuum microelectronics attract attentions from many research fields. In all kinds of applications of the vacuum microelectronics, field emission display (FED) is one of the most producible products with competitive advantages in near future. Several kinds of the cathode with different materials and structures in field emission devices have been developed recently. The “Spindt-type” structure was first proposed by C.A. Spindt in 1968 [1]. It has been reported that it is one of the most promising structures to fabricate an electron emitter with low turn-on voltage. The planar also attract much interest in the application of field emission displays, such as surface conduction electron emitter (SCE). Surface conduction emission is the phenomenon that electrons are embittered from a cathode when electric current flows through the cathode in parallel with the cathode surface [2]. Diamond-Like Carbon (DLC) was another popular material which can operate at relative low electric field [3].

Since the first observation of carbon nanotubes (CNTs) in 1991 by Iijima [3], CNTs have attracted a great deal of attention from many research groups resulting from their unique chemical and physical properties, such as high aspect ratio, high mechanical strength, chemical inertness, large current capability and high thermal conductivity. CNTs have been considered to be an excellent material for electron emitters in FED.

The common methods of CNT synthesis are arc discharge [4], laser ablation [5], and Chemical Vapor Deposition (CVD) [6~10]. However, the arc discharge and laser ablation have the drawbacks of high thermal budget, low throughput, and non-uniformity in synthesis. In contrast, CVD appears to be a good technique in synthesis of CNTs for its simplicity and scalability. Therefore, recently many researchers have devoted themselves to the development of CVD techniques for synthesis of CNTs in pure quality and high quantity. However, low temperature growth condition and uniform emission characteristics are unavoidable in FEDs. In this experiment, the characteristics of the field emission device were improved by **c**o-deposited catalysts and pillar-like pattern. Co-Ti/Al layers have been utilized as a catalyst for the growth of pillar-like CNTs in a thermal-CVD system. Compositing theirs advantages improve the field emission characteristic and reliability of the sample.

Experimental

The fabrication procedures of patterned CNT emitters were showed schematically in Figure 1. A Chromium (Cr) layer (100nm) was deposited on the 4 inch (100) n-type wafer by E-gun evaporation (JAPAN ULVAC EBX-10) as the cathode between the substrate and catalyst (Fig.1 (a)). Afterward, a photoresist was spin-coated on Cr layer and the emitting sites were defined by mask which has several 6μm diameter circles with interspacing of 30μm by photolithography (Fig.1 (b) ~ (c)). And then, 20Å cobalt (Co) and 30Å titanium (Ti) co-deposited on 100Å aluminum (Al) as catalysts were deposited by magnetron sputtering (Ion Tech Microvac 450CB) (Fig.1 (d)). The patterns were formed after removing the photoresist by lift-off method. Finally, pillar-like CNTs were grown selectively by thermal CVD system: the sample was pretreated at 550 ℃ (Fig.1 (e)) and then grew CNTs (Fig.1 (f)). Another sample was fabricated as a contrast. The procedures of the sample were the same as Co-Ti/Al sample except that catalysts were replaced by multi-layers: 20Å Co and 30Å Ti. The processes of CNTs synthesis were showed in Figure 2. The pretreatment condition was injected into the quartz with hydrogen flow (H_2) (50 sccm) about 5 minutes to reduce the catalyst metal to the metallic phase and transform into nano-particles [11]. While CNTs were grown in the quartz, the gases flow rates were 10 sccm for hydrogen, 100 sccm for nitrogen (N_2) and 125 sccm for ethylene (C_2H_4) in there at 550 ^{o}C.

Electric characteristics of CNTs field emission were measured with a parallel diode-type configuration in a high-vacuum chamber with the pressure of 5×10^{-6} Torr. A glass substrate coated with indium tin oxide (ITO) and P22 phosphor (ZnS: Cu, Al) was used as the anode plate, and the distance between the cathode and the anode plate was set to be 150 μm. The emitting area was variable, which was determined by pillar-spacing and pattern-area. The vacuum measurement system was showed in Figure 3.

Anode voltages are sweep-type from 0 V to 1000 V which were applied at intervals of 10 V with a source measure unit (Keithley 237), as Figure 3 for the verification of field emission characteristics while the cathode was biased at 0 V.

Result and discussion

The differences between two samples were methods of deposition for catalysts. Figure 4 (a) and (b) showed the atomic force microscope (AFM) images of the Co/Ti/Al catalysts and Co-Ti/Al catalysts during pretreatment process. The particle size and RMS were inscribed in Table 1. In this experiment, the Al layer plays the role of increasing RMS and increasing planar density of catalyst particle to improve CNTs had superior profile, density, and edge. Therefore, the RMS were almost the same because the determined factor was the 100Å Al under the Co-Ti or Co/Ti catalyst films. However, owing to the existence of the co-deposited Ti, the coalescence of the Co nano-particles was retarded and suppressed during the pretreatment. Hence, the co-deposited catalytic nano-particles were smaller, more uniformly distributed, and more stable than the multi-layer catalytic nano-particles [12].

The pillar-like structure was used to reduce the screening effect due to each pillar can be regarded as an individual emitter. Figure 4 (c) and (d) were showing the Scanning Electron Microscope (SEM) images of the pillar-like CNTs growing by Co/Ti/Al catalysts and Co-Ti/Al catalysts. From the SEM images, the sample with Co-Ti/Al catalysts was more aligned than the sample with Co/Ti/Al catalysts. On the other hand, the Raman spectra were used to investigate the graphite structure of the samples (Figure 5 (a)). According the Raman spectra, the sample with Co-Ti/Al catalysts of the I_D/I_G rate was lower than the sample with Co/Ti/Al catalysts. Figure 5 (b) listed the values of the I_D/I_G rate in two samples. It explained the graphite structure of the Co-Ti/Al catalysts sample was better than Co/Ti/Al catalysts sample. For multi-layer catalysts film, we explained that by surface energy of interface, the most effective factor is the melting point and difference of surface energy. But for co-deposited catalyst film, we took it as an alloy or solid solution, it meant the constituent is uniform as same as other alloy. Therefore, the co-deposited catalysts may form the better graphite and alignment structure than multi-layer catalysts at low growth temperature. That is to say the co-deposited catalysts could effectively decrease the growth temperature of CNTs to 550℃ [13].

Composing the above reasons, the Co-Ti/Al catalytic sample had better field emission characteristic and reliability. Figure 6 was showing the field emission characteristic of two samples. Table 1 revealed the current densities of the Co-Ti/Al catalytic sample and the Co/Ti/Al catalytic sample were 1272 $\mu A/cm^2$ and 1124 $\mu A/cm^2$ at 6 V/μm. The turn-on fields were 3.6 V/μm and 4.4 V/μm in the Co-Ti/Al catalytic sample and Co/Ti/Al catalytic sample. Stress experimental tests were used for testing the life time of a backlight unit. In our researches, the stress test was always under the 1000V (6.78 V/μm) and keep a long time (2 hours). Figure 7 and Table 2 showed the reliabilities of two samples. The advantage of co-deposited catalytic film appeared evidently, the current variation of pillar-like CNTs on Co-Ti/Al was only 7% of initial value. As a result, the co-deposited catalyst not only improved the I-V characters but also increased the reliability of pillar-like CNTs.

Conclusion

We proposed the pillar-like CNT field emission arrays synthesis with co-deposited multilayer catalyst at low temperature. The sample had better properties due to composite the advantages of Al layer, co-deposited, and pillar-like shape. The current density of the sample was as high as 1272 $\mu A/cm^2$ at 6 V/μm and the turn-on field was 3.6 V/μm. Additionally, the reliability was more stable as lower than 7% degradation of initial current density.

Acknowledgement

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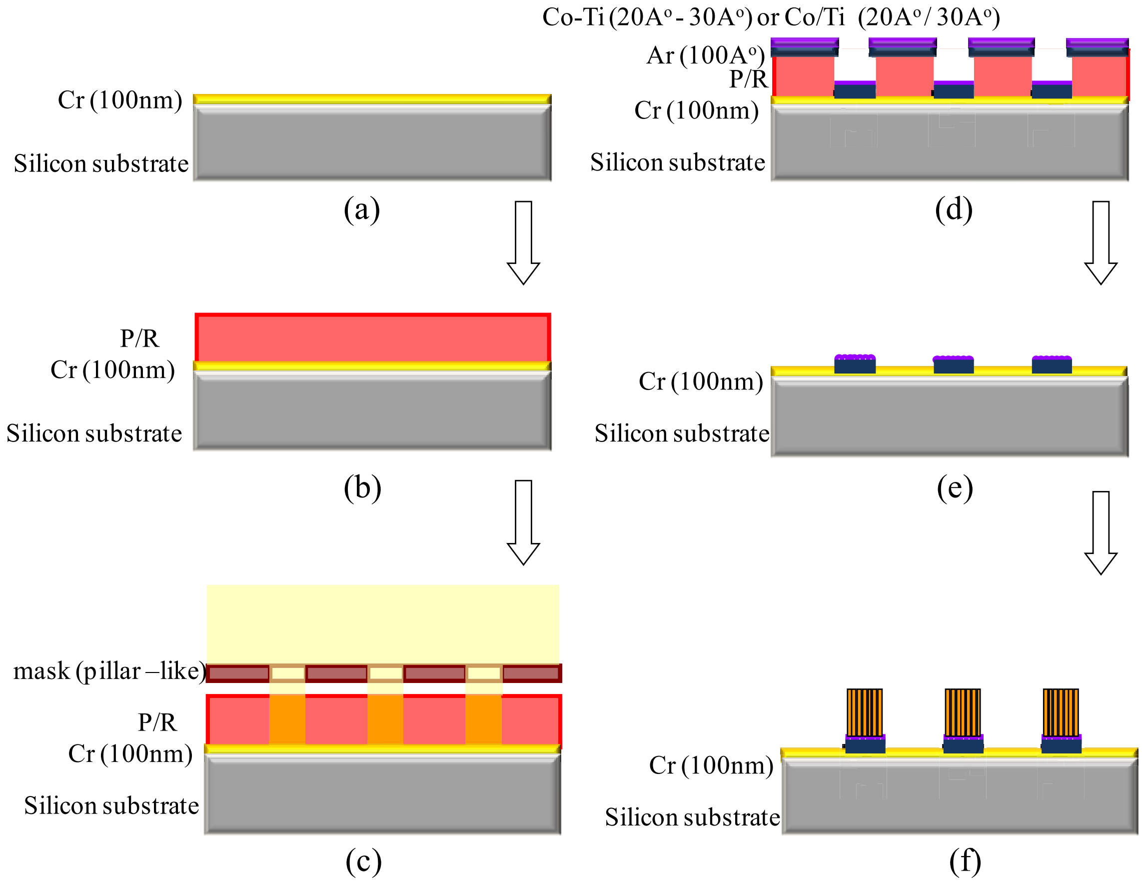


Fig. 1 A schematic diagram of the fabrication procedure

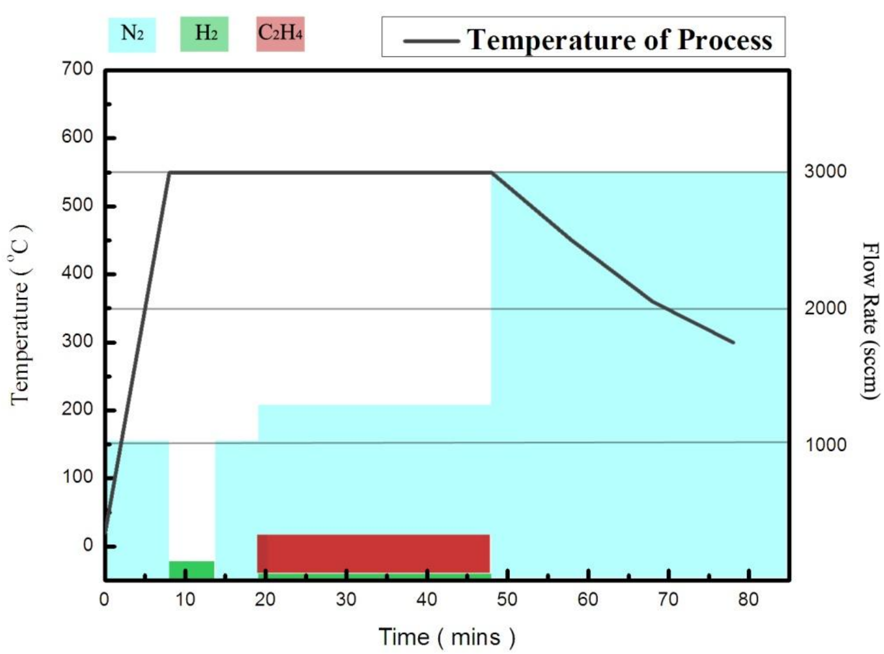


Fig. 2 The processes of CNTs synthesis

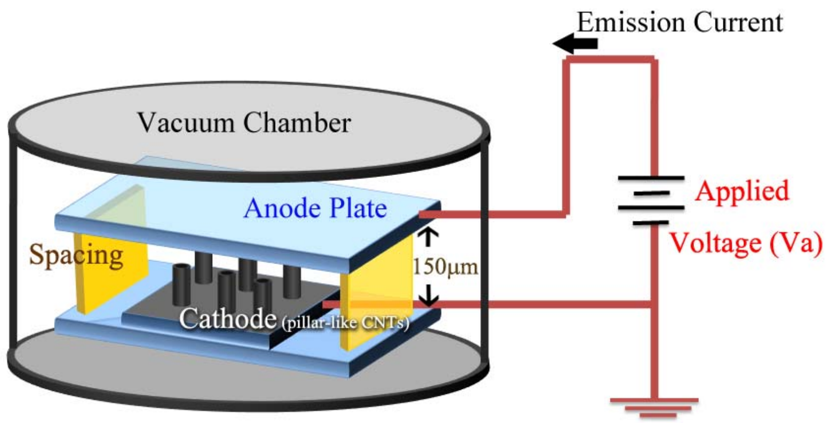


Fig. 3 High vacuum measurement system

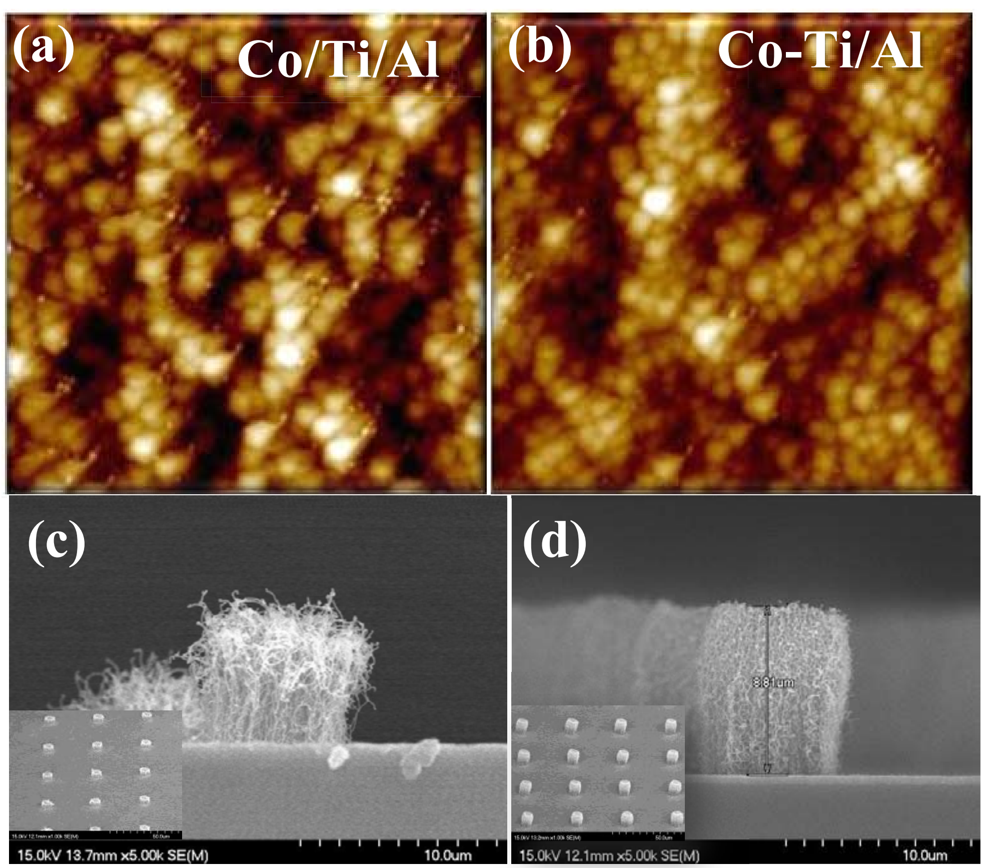
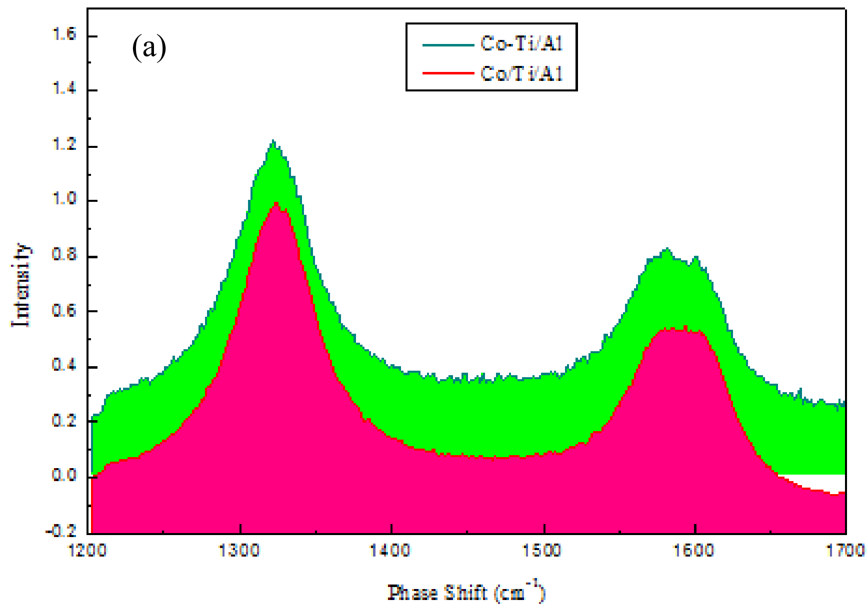


Fig. 4 AFM image of the particle during pretreatment. (a) Co/Ti/Al (b) Co-Ti/Al SEM image of the pillar-like structure (c) Co/Ti/Al (b) Co-Ti/Al at 550 °C



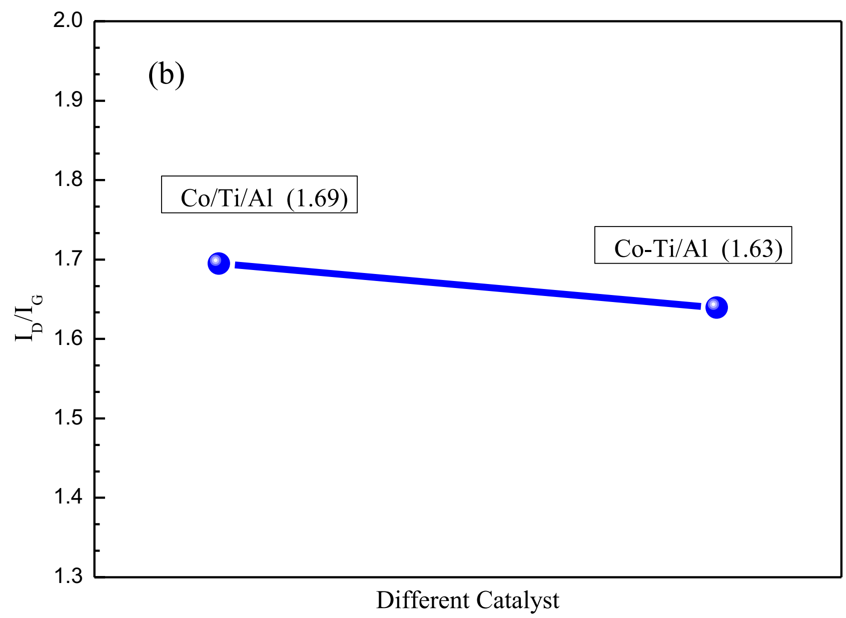


Fig. 5 (a) Raman spectra of two samples (b) the I_D/I_G rate of two samples

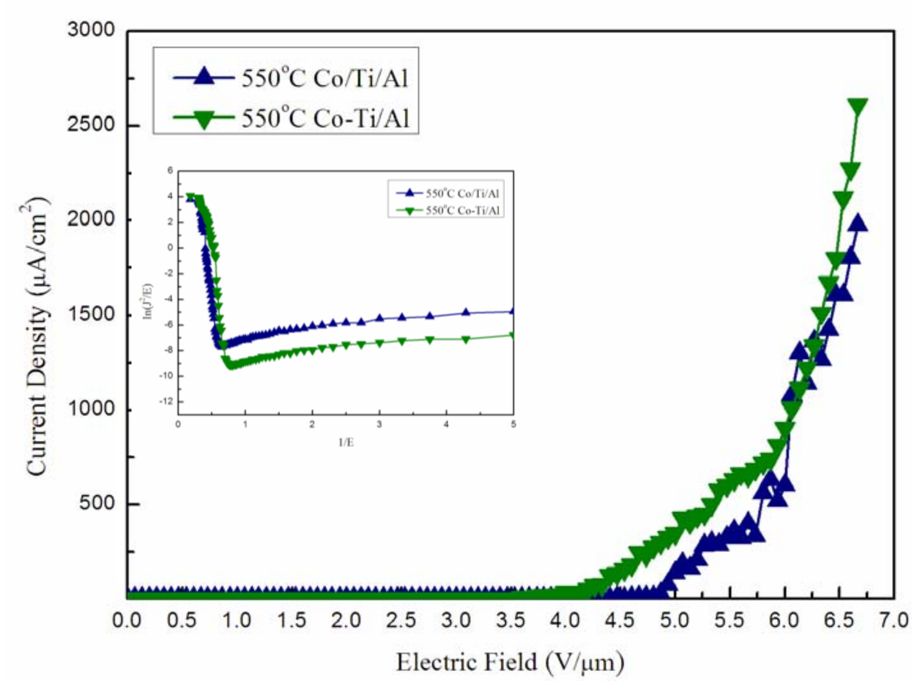


Fig. 6 J-E characteristic of two samples (insert figure is the FN plots of two samples)

Table 1 RMS and particle size of two samples during pretreatment and the field emission characteristic of two samples

550 °C	RMS (nm)	Particle (nm)	Turn-on (μA/cm²)	At 6 V/μm (μA/cm²)
Co/Ti/Al	7.972	75	4.4	1124
Co-Ti/Al	8.358	65	3.6	1272

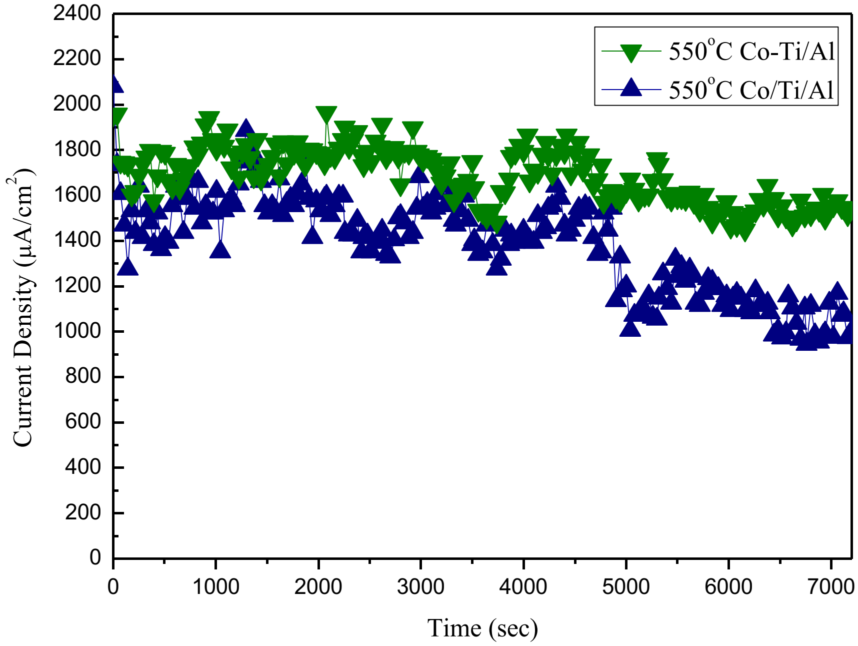


Fig. 7 The reliability of two samples

Table 2 reliability of two samples at 550 °C

550 °C	Average (uA/cm²)	Variation (% of fluctuation)	Degradation (% of initial value)
Co/Ti/Al	1385	14.6	20.0
Co-Ti/Al	1688	7.0	11.4