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Novel field emission emitters with nanoscale tips based on Mo oxide fabricated by electrochemical methods

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Abstract

Novel-structured field emission emitters with nanoscale tips and a fabrication technique using a nanoscale gap are described. The fabrication technique makes it possible to form the emitters on a meter-scale glass substrate. The emitter has a configuration with one side gate to reduce the electron scattering losses at the counter electrode in order to improve the emission efficiency. All thin film layers constituting the emitter were fabricated by plasma CVD and sputtering deposition methods. Nanoscale tips were formed between a shallow gap less than 7nm deep by using joule heating of Mo complex oxide, which was produced by electrochemical etching of a deposited Mo layer. To our knowledge, this is the first work that shows a uniform efficiency of 5% or more achieved under the conditions of an anode voltage of 10KV and operation voltage of 23V .

1. Introduction

Field emission emitters which have a capability of being driven by a low voltage, formed over a large area [1] and exhibit a low fluctuation of electron emission are of interest for practical field emission displays (FEDs)[2]. A surface conductive emission emitter (SCE) [3], which could be operated at voltages of less than 22V and formed on a glass substrate of meter scale has been previously demonstrated. The electron emission efficiency, η, for an SCE is defined as below.

$$\eta = \frac{I_e}{I_f + I_e}$$

I_e : electron emission current achieved anode electrode
I_f : film current between cathode and gate electrode

The efficiency of the SCE was less than 1.0% at an anode voltage of 10kV. Therefore, an improvement of emission efficiency is needed in order to reduce the thickness of Cu wiring layers.

Efficiency can be improved by reducing the number of electrons on the surface of the counter electrode scatter. In order to reduce the number of scattering events, the local electric field in the vicinity of the gap is reduced by an appropriate design of the electrode structure. This device is called a vertical-type surface emission device (V-SED). In this paper, the macrostructure of the device, and the fabrication process of the nanoscale gap and tips of the V-SED are described.

2. Device structure

Figure 1 shows a V-SED emitter array with cathode bus lines and gate bus lines. The image is a composite of an optical microscope image and a luminescence image associated with tunneling electron emission. The size of the array is 210x630μm^2. Each of the 52 cathodes has an 8μm width and a comb like structure. Figure 2 shows the configuration of the V-SED. The device is composed of thin films, a glass substrate, and SiN (500nm), SiO_2 (25nm), Ta (40nm), and Mo (30nm) layers. The film layer of SiN is deposited by a plasma CVD method. Other film layers are deposited by sputtering methods. Electron emission tips are formed on the cathode and extend between the cathode and the gate. The notch length from the open space is on the order of 100nm.

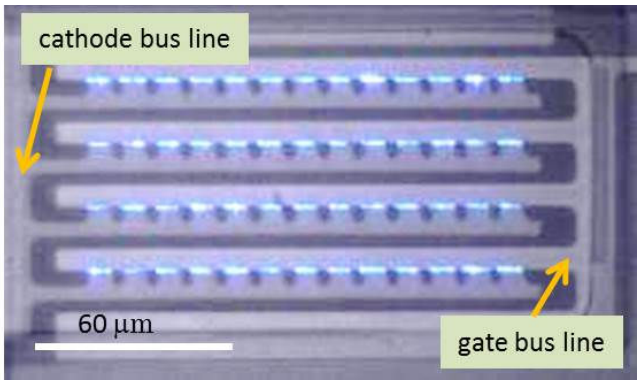

Fig. 1. Composite optical microscope and luminescence image with tunneling current of 23V..

In order to achieve low driving voltage (<25V), the V-SED is fabricated by a two-step process: formation of a wide gap less than 25nm and formation of a narrow gap of less than 10 nm. The wide gap was obtained by partially removing the SiO_2 layer by buffered hydrogen fluoride (BHF) etching. The narrow gap is obtained by electrical joule heating the Mo complex oxide, which is electrochemically generated by using tetramethylammonium hydroxide (TMAH) etchant. The volume and the resistivity of Mo complex oxide are controlled by the oxidation condition (120°C in air) after Mo layer deposition.

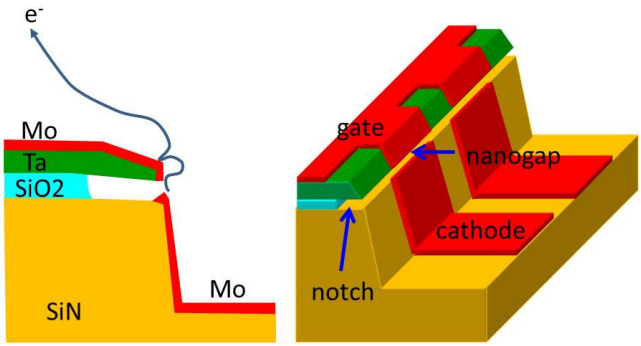

Fig. 2. Schematic diagram of V-SED structure.

The right side of Figure 3 shows a SEM image of the V-SED. The top left image of Figure 3 is a SEM image of the nanogap between a cathode and an anode before vacuum baking (400°C). Discrete nanoscale Mo-based electron emission structures are generated and there are short-circuits between the cathode and the anode. This is called a nano bridge. The detailed fabrication mechanism of the nanobridge is not yet clear, but it is speculated that generation of the nanobridge is produced by the cell reaction occurring between the Cu wiring material and Mo cathode electrode at TMAH etching. Material composition of the Mo surface, including the nanobridge, is detected as complex oxide peaks of MoO_2, MoO_x ($2<x<3$) and MoO_3 analyzed by the X-ray Photoelectron Spectroscopy (XPS) method. After vacuum baking, a voltage of 23V is applied between the extracted gate and cathode lines so that the nanobridge is destroyed in the middle. The bottom left image of Figure 3 is a SEM image showing the nanoscale emission tips on the cathode's edge. The nanogaps between the end of the tip and the gate are estimated to be narrower than 7nm.

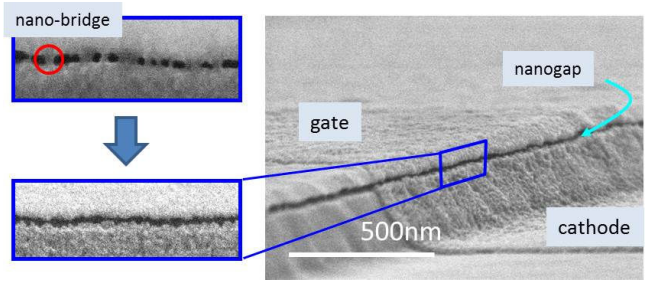

Fig. 3. Nanotip emitter fabricated by I-V joule heating method.

The transection of the V-SED is observed by using high–angle annular dark field scanning TEM (HAADF-STEM) in order to investigate the shape of the electron emitter inside the notch. Figure 4 shows that the electron emitter of the V-SED is a ~20nm-high tip pointing toward the gate electrode. The center of the tip has high density and is covered with low-density materials.

The elemental composition of emission material is investigated by electron energy-loss spectroscopy (EELS) with Mo (M_3-edge, red), O (K-edge, blue), and N (K-edge, green) mapping. Examination of the peak of energy loss reveals that the center of the tip is composed of metallic Mo and is covered with the mixed oxides of MoO_2 and MoO_3. In terms of conductivity, most of the surface of the electron emitter is not likely MoO_3 because MoO_3 is an insulator. On the other hand, MoO_2 is a semiconductor material, so it can be assumed that most of the surface of the tips is mainly composed of MoO_2. The work function of MoO_2 is relatively high (5.8eV). Therefore, the more reduced oxides, MoO [4], can be expected by the desorption of oxygen from MoO_2 owing to the heat from electron emission.

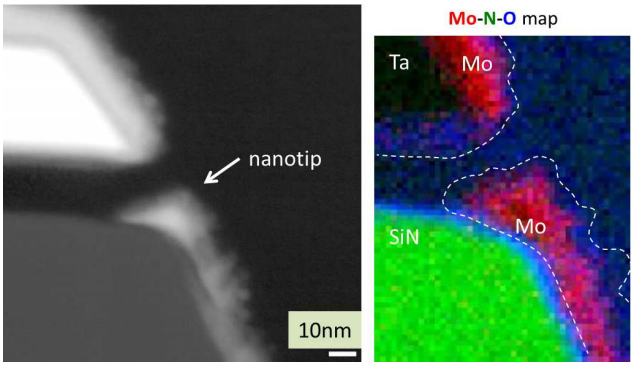

Fig. 4. HAADF-STEM image of notch area. Right image shows atomic mapping by EELS.

3. Conclusions

As is shown in Fig.1, blue luminescence with intensity proportional to field emission current[5] is observed. Good uniformity of emission intensity is confirmed. This uniform intensity means all cathodes in the device have uniform tunneling current. Electron emission current of about 12 μA with fluctuation of 0.6% and emission efficiency of 5% were achieved when this V-FED was driven by 23V, 230μA film current and 10kV anode voltage.

This result indicates that the V-SED configuration is promising for an electron emitter in high-efficiency FED and that it is possible for the nanoscale gap device to be manufactured uniformly on large glass substrate.

References

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