Purification of Pt EBID Structures by in-situ Annealing with Electron Beam Post-irradiation under Oxygen Flux

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ABSTRACT

Direct deposition of purely metallic structures is difficult to achieve by electron beam induced deposition (EBID) process. Typically, a precursor such as $MeCpPtMe_3$ leads to carbon-rich EBID structures with 15 at.% Pt and a value of resistivity nearly six orders of magnitude higher than that of pure bulk Pt. We have purified the Pt structures by a combinational post-treatment: in-situ annealing with electron beam irradiation under oxygen flux at annealing temperature of 120°C. An electrical contact of desired dimensions is fabricated by stacking up individually purified thin Pt structures on top of one another. The I-V curve measured for a single thin structure, before and after purification, shows a significant decrease in the resistance of the structure upon purification. The I-V curves measured for five successive layer of pure Pt show a successive consequent decrease of the resistance, with increase of the thickness of the contact. So the method allows the creation of highly conducting contacts with a free choice of engineering dimensions in x, y and z.

Keywords: EBID structures, purification, Pt, e^- beam irradiation, oxygen

1 INTRODUCTION

Although micro-nano structures of a variety of materials can be deposited with the Electron Beam Induced Deposition (EBID) process with good control over the pattern definition [1,2], the low purity of the deposits is a general shortcoming. The structures deposited with organometallic precursors such as $MeCpPtMe_3$ contain only 15 at.% Pt. Purification of such structures is necessary to enhance their performance as metallic contacts with sufficiently low resistivity. Different post-treatments [3] including post-deposition annealing in the presence of oxygen [4] and electron beam (e^- beam) post-irradiation are effective post-treatments for partial carbon removal [5], however, the use of a high annealing temperature may distort the pattern definition. In addition the e^- beam post exposure is effective only for very thin EBID structures. We have used a new combinational post-treatment in-situ annealing with electron beam irradiation under oxygen flux to purify thin Pt structures. A sequential approach of deposition and purification of thin Pt structure on a previously purified Pt structure has been followed to fabricate a pure Pt structure of desired dimensions.

An electrical contact is fabricated by stacking up five thin purified Pt structures and the I-V curve is recorded each time a new layer has been purified. These measurements will be helpful to optimize the sequential deposition purification process for fabrication of electrical contacts as per the requirement of each specific application.

2 EXPERIMENT

The Pt structures are deposited on Si substrate with few nm layer of native oxide in a FEI NovaNanolab DualBeam instrument. For fabrication of pure Pt structure by sequential approach, thin (< 100 nm) Pt structures are deposited at 120°C with an e^- beam of 5kV, 1.6 nA and then post-irradiated with an e^- beam of 5kV, 24 nA at 120°C while oxygen is flooded in the close vicinity of the substrate via a gas injection system (GIS). More experimental details are reported in another publication [6]. A Keithley system source meter 2636A is used for electrical 4 point probe measurements using Pt depositions on a predefined Au patterned substrate (Au on SiO2 on Si). All the electrical measurements are done in-situ.

3 RESULTS

3.1 Sequential Deposition and Purification of Pt Structures

Incomplete dissociation of the precursor molecules upon impact with e^- beam is one of the main causes for having a carbon–rich EBID structure. When such structures are exposed to a combination of the e^- beam and oxygen at elevated temperature, the e^- beam and increase in substrate temperature help further dissociation of the partially dissociated fragments of the precursor molecule. The volatile compounds of carbon formed after interaction with oxygen are then pumped away. It has been observed that the lateral dimension of the structure purified by this post-treatment were not greatly affected but the height of the structure was reduced and the morphology of the structure was a mix of voids and pure Pt grains, as an effect of carbon removal.

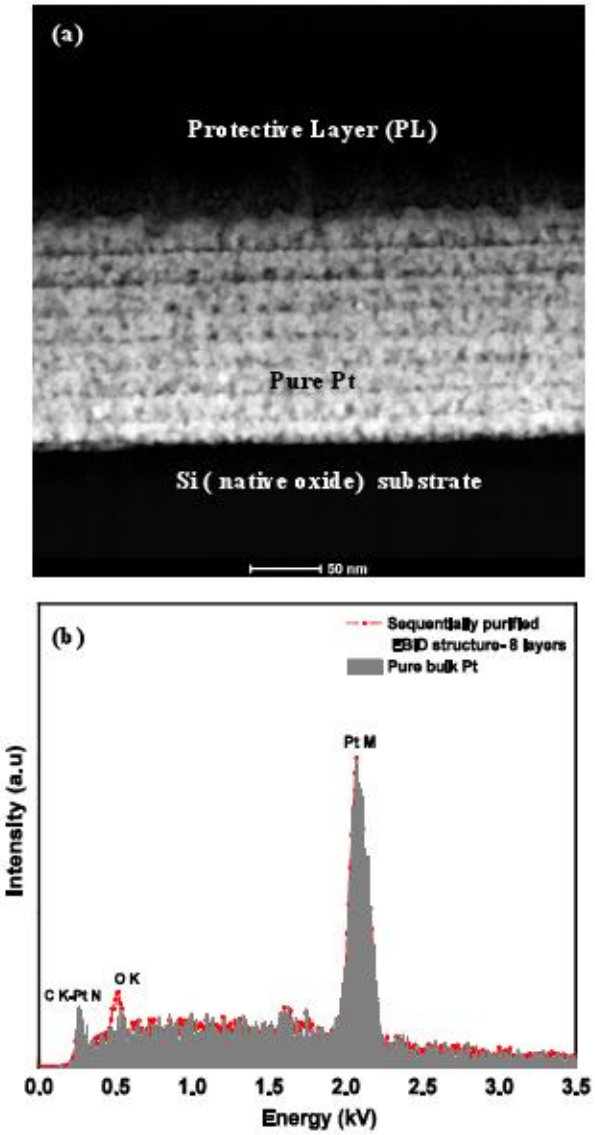

Figure 1: (a) STEM micrograph of pure Pt structure fabricated by sequential deposition and purification. (b) EDX spectra of pure bulk Pt and the purified structure. The spectra are normalized w.r.t Pt M line.

A thin Pt EBID structure (2µm x 2µm x 60 nm) can be completely purified after a prolonged e^- beam irradiation (5kV, 24 nA, 25 minutes) at 120°C under oxygen flux. An identical thin Pt structure is deposited on this previously purified structure and post-treated. A pure Pt structure of final dimensions (2µm x 2µm x 160 nm) as shown in Figure 1(a) was fabricated by stacking up eight such thin pure Pt structures. The final height of the structure is nearly 33% of the height of an equivalent as deposited. As a new structure is deposited on a previously purified one, the voids in the bottom layers are filled, making a dense layer of pure Pt. The comparison between EDX spectra of this structure and pure bulk Pt reveals that the structure has been completely purified. The EDX and PEELS signal corresponding to oxygen measured across the thickness of the structure suggest that the O K line peak in the spectrum correspond to the additional oxidation of the substrate. More details about purification of Pt structures by this post-treatment are reported in [6].

3.2 Electrical Measurements

In order to optimize the fabrication of a contact by sequential approach, it will be very helpful to know the resistance of each thin layer of Pt as the contact is being formed. We have used a pre-patterned four point probe structure with 200 nm thick Au pads on a 200 nm SiO_2/ Si wafer. The Au pads were slightly thinned by focused Ga^+ion beam milling. A contact of 1µm x 15µm made up of five thin Pt layers with estimated final thickness of approximately 90 nm was fabricated by sequential deposition and purification at 120°C in similar manner explained in the previous sub-section.

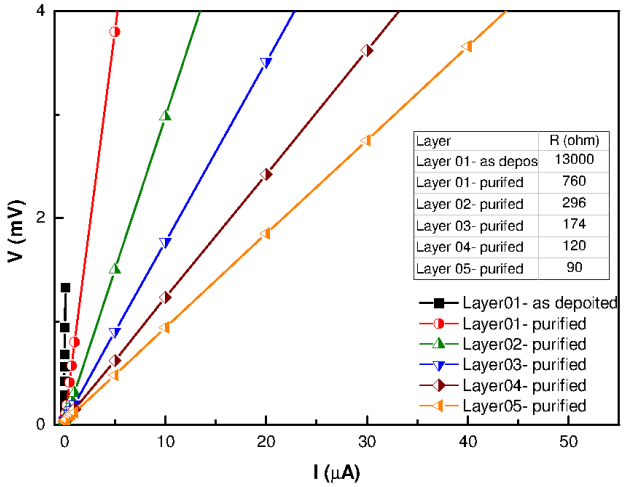

Figure 2: Graph of voltage vs. current for each layer of the contact fabricated by sequential deposition and purification.

For the measurement of resistance, a current between 50µA and 1 nA was passed through the contact. The measurements are done in-situ when the structure was kept at 120°C. The pressure inside the chamber was around 2 $x10^{-6}$ mbar. The resistance of the thin layer of Pt before purification is nearly 13kΩ which reduces to around 760Ω after purification of that specific layer. An identical Pt structure was deposited on top of the purified one, sequentially purified and electrical measurements were repeated. It has been observed that the resistance is decreasing after addition of each purified Pt layer to the contact while the relative decrease in resistance between two consecutive layers reduces with addition of layers, hence increase in the thickness of the contact. This trend is very much expected from the observation made in the previous subsection. As the number of layers which make the electrical contact increase, the voids in the bottom

layers are being filled up with pure Pt grains. As the bottom part of the structure is denser, the electrical contact will be better, hence the resistance decreases with the number of layers.

4 CONCLUSION

The post-treatment: in-situ annealing with electron beam irradiation under oxygen flux is an effective method for purification of Pt structures. A pure Pt structure of desired dimensions can be fabricated by sequential deposition and purification approach. The resistance of the structure reduces by two orders of magnitude upon purification. A contact of 1 µm x 15 µm with estimated final thickness of 90 nm consisting of five thin layers of pure Pt has a resistance of 90 Ω. These electrical measurements will provide some guideline for further optimization of the process depending on the application of the contact.

5 OUTLOOK

The method described above has been applied to a precursor where the dissociation can never result in pure volatile and non-volatile parts. The addition of oxygen is assumed to allow the released carbon to leave the surface as either CO or CO_2, while not oxidizing the platinum. For this reason the method is assumed to be applicable to other deposition processes involving carbon rich precursors and noble metals such as gold or palladium. These precursors and their deposition processes / purification schemes, are the subject of study in the near future. In addition for non-noble metals the method may be used to produce oxides of proper stochiometry and low carbon content.

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