Immersion Nickel Deposition on Blank Silicon in Aqueous Solution Containing Ammonium Fluoride

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Abstract

Immersion deposition of Ni on p-Si (100) blank substrates was carried out in an aqueous $NiSO_4$ solution at a pH value of 8 through displacement reactions. Study of the early deposition stage revealed that incorporation of 2.5M NH_4F in solution promoted Ni nucleation significantly. By adding fluoride, it was observed that metallic Ni was deposited constantly at the expense of Si and the deposition was not self-limited. Sponge-like Ni deposits were observed and it might explain the non-limiting feature of such immersion Ni deposition over Si. Transmission electron microscopic images of Ni/Si cross-sections showed that during the reactions, Si oxide played a role of the intermediate phase. The whole process could have involved successive Si oxidation steps. Eventually the oxide was etched away by fluoride resulting in a nanoporous Ni film.

Keywords: Nickel; Ammonium fluoride; Transmission electron microscopy; Chemical deposition

1. Introduction

When using a wet method for certain fabrications, it is both desirable and convenient to have deposition produced on the sample surface with no need of electrical contacts, thus allowing deposition by simple immersion of the sample in a solution containing appropriate metallic ions. Therefore, electroless plating is universally utilized. For example, it is now applied extensively in electronic processing [1, 2]. Recently wafer-scale fabrication of metallic structures on Si surface has become one of the key technologies to develop various nanoscale devices [3-5]. Takano et al. in particular have

introduced an electroless Ni bath without reducing agent for immersion Ni deposition on Si (100) aiming for fabricating fine metal dot arrays. They found that displacement reactions including cathodic and anodic redox couples had taken place between the Si atoms on surface and the Ni ions in solution [6-8]. F. A. Harraz et al. studied the immersion Ni behavior on porous Si to establish electrical contact for full realization of the porous Si device [9]. In addition, Gorostiza et al. reported the electrochemical study of immersion Ni deposition at open-circuit potential on Si in both acidic and alkaline fluoride solutions and discussed the involved charge exchange processes [10]. We have adopted a similar Ni bath for metallization of arrays of ultra-high-aspect-ratio macropores that were etched by HF onto selective regions of p-type Si substrates. In this way, we can build up an inlaid conductive structure in Si for application to radio frequency cross-talk reduction in mixed signal integrated circuits [11]. In order to better understand the Ni and Si interaction during the process, typically for a long duration, immersion deposition of Ni on blank Si has been investigated in this study using an aqueous $NiSO_4$ solution containing 2.5 M ammonium fluoride but no conventional reducing agent. Both the initial stage and the long term immersion had been looked into. Electron microscopic work was conducted to observe the resultant surfaces and cross-sections.

2. Experimental details

The substrates used in this study were square pieces of 2 cm × 2 cm cut from p^- type Si (100) wafers with resistivity ~ 10 Ω cm. These Si samples were cleaned by RCA method [12], using successively a mixture of 1 part of NH_3H_2O, 1 part of H_2O_2 and 5 part of H_2O for 15 min, and then a 2%-HF solution for 2 min. After cleaning, the samples were rinsed in deionized water (18 MΩ cm), which was used in all stages of the experiments.

Firstly, two types of baths were prepared as listed in Table 1 in order to compare the early stage of Ni immersion deposition on Si. The difference between baths, as can be seen, is that one was with NH_4F added and the other without. However, both contained a fixed concentration of $NiSO_4$ (0.1 M) for supplying Ni^{+2} ions and $(NH_4)_2SO_4$ (0.5 M) for serving as the buffer. Baths were adjusted to an alkaline state with pH value of 8. This is because hardly any observable Ni deposition was found in solutions with an acidic state [10]. The temperature was 80º C. Effect of the presence of NH_4F in promoting nucleation and deposition for the initial 5 min was demonstrated by atomic force microscopic scanning of the treated substrate surface areas. (AFM; Nanoscope II, Digital instruments, Inc.)

In the second round experiments, by immersing the Si samples in a bath of 1.0 M $NiSO_4$ with the same amount of fluoride for an extended time of 8 h, Ni deposits on Si were examined by field emission gun scanning electron microscope (FEGSEM; JOEL JSM 6700) equipped with energy dispersive X-ray spectrometer (EDX or EDS; Kevex Instruments, Inc., Sigma). Specimen cross-sections were thinned down in a metallurgical

way for subsequent observation under a field emission transmission electron microscope (TEM; FEI/Philips CM200). Thus we could be provided with the details of the immersion deposition which occurred at the interface between Si substrate and fluoride-containing Ni electrolyte.

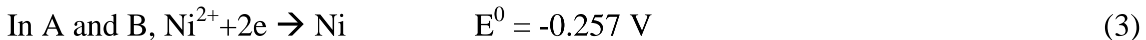
3. Results and discussion

3.1. Effect of NH_4F on the initial immersion Ni deposition process on Si surfaces

In a previous study, it was found that immersion Ni deposition on Si could take place in a simple solution containing only $NiSO_4$ and $(NH_4)_2SO_4$ without reducing agent [3]. It is based on a displacement principle that can be applied to other metal ions in similar solutions. Usually such electrolytes containing HF were used as well while working with the semiconductor surfaces for enhanced immersion deposition [13-17]. When HF is added to the Ni bath, induced low pH value does not promote Ni deposition on Si [9, 10]. Therefore, NH_4F was added to achieve an alkaline state in the Ni bath. With two electrolytes A and B listed in Table 1, we are able to demonstrate the effect of NH_4F on immersion Ni deposition on Si with comparison to case without the NH_4F. Fig. 1 shows two AFM images of early deposition, respectively for 5 min Si immersion in bath A and B. The images characteristic to each plating bath and were taken by scanning a surface area of 400 μm^2. Apparently, for a given time, the amount of deposits increased due to the existence of concentrated fluoride in bath B. NH_4F significantly enhanced Ni nucleation and total deposition. Regardless of the pH value which could be kinetically important during the process, we can at a first glance consider the difference in driving forces between these two processes from a thermodynamic point of view. We describe each of the deposition processes in general by a couple of redox reactions in the following [18].

In A, $Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^-$ $\quad E^0 = -0.84$ V (1)

In B, $Si + 6F^- (aq) \rightarrow SiF_6^{2-} (aq) + 4e^-$ $\quad E^0 = -1.20$ V (2)



In A and B, $Ni^{2+} + 2e \rightarrow Ni$ $\quad E^0 = -0.257$ V (3)

According to the redox potential values, we can see that process in B is more favorable due to a higher driving potential for the electrons to be transported from Si to Ni. Nevertheless while an enhanced amount of deposits was displayed in the early stage with the presence of NH_4F, we could not observe distinguishably large Ni particles grown in size. From both AFM images in Fig. 1, we could find out that deposited particles from both processes are of approximate height. This should agree to the assumption that Ni is reduced at the expense of Si on the surface. Therefore particle formation is more

dominant than particle growth until a continuous layer of deposits forms. From a kinetic point of view, an alkaline solution containing fluoride was able to give rise to highly corrosive surface sites and thus enhance the metal deposition [19].

3.2. Long-duration immersion of Si in the Ni bath with NH_4F

So far it is commonly understood that immersion (or displacement) deposition continues as long as the substrate material is removed and its by-products can diffuse throughout the porous regions in the layer of deposits. But eventually the process is self-limiting [20]. As pointed out in the preceding discussion, Ni deposition in the initial stage occurred preferentially by nucleation on Si surface rather than building up the as-formed Ni particles. It was suggested that once a layer of deposits was formed, deposition would thereafter proceed to the second layer over the first one resulting in less uniform particle sizes and contribute to an enhanced surface roughness [15]. So far, little experiment has been reported upon a long-term situation of such deposition.

After 8-hr immersion in $NiSO_4$ bath with NH_4F, the surface with deposits was shown in Fig. 2a, the scanning electron microscopic image. Apart from the roughness, noticeable features were that Ni deposits were made of aggregated ultra fine particles and assumed a sponge-like structure. The first feature was directly pertinent to the abundant nucleation behavior during the displacement process. The second should be resulted from the fluorine ions in the bath causing certain reactions and thus probably leaving interconnected voids inside. This point will be elaborated on in the next few paragraphs. Void space inside the cluster of deposits may provide open channels for reactive species to be transported from the solution and allow further oxidation and reduction inward. In this way more Si underneath was consumed and Ni deposits were thickened. These speculated processes were confirmed by observing the specimen interface with the Ni coatings peeled off, as shown in Fig. 2b and c. Apparently after hours, immersion Ni deposition via displacement reactions was still progressing below the as-formed layer of deposits. It infers that the Ni deposition over Si was not yet self-limited up to hours long most probably because of the sponged structure. That is to say, deposits could grow up via successful removal of reaction by-product generating a porous structure. Reactive species were imported from the solution through these pores for progressive reactions, i.e. Si oxidation and Ni reduction. However, the deposition might be gradually retarded due to increasing difficulty for mass transport through narrow channels.

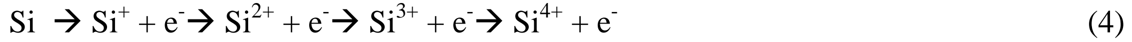
Taking off the as-deposited layer, we were able to look closely at the exposed surface which had been the interface between deposits and substrate. From there, we indeed investigated more immersion Ni deposition over Si through progressive displacement reaction couples in an aqueous bath. SEM micrographs in Fig. 3 show that at certain sites on surface (the original interface), Ni deposition continued based on the suggested

general equations of displacement reactions. Further observable inside the roughly round-shaped areas, Si oxidation was along with Ni reduction. In Fig. 3a, verification by the energy dispersive X-ray spectroscopy was conducted to acquire elemental ratio of Ni:Si:O as 65:30:5 (wt.%). Tiny Ni deposits were nucleated and embedded within the oxidized Si. Sequentially in Fig. 3b more Si oxidation enlarged the reaction sites and more Ni deposition was accordingly caused covering gradually from the center over the Si oxide which expanded on the edge simultaneously. Previously studied in a similar Ni bath with no fluoride, formation of Si oxide species initiated the Ni deposition [21]. It was proposed that oxidation of Si served as “reductant” for Ni ions. As a result, rather than a complete Ni layer, Si dioxide was the other phase that had been found existent in the deposits [21]. In that process, Si could be successively oxidized while electrons kept being released for spontaneous metal reduction onto or into the oxide. Eventually the deposition was ceased due to the passivity of Si dioxide. Comparatively, the Ni deposits from our experiment was of loose structure that spread from right middle where the reactions had started. Most likely Si dioxide initiated originally in the center of reaction sites had already been etched away by F^- ions in the solution. Dioxide could be formed by means of full Si oxidation during the process and finally removed by fluoride. In a way, a combination oxidation and dissolution should stand for the second equation proposed in the previous text. The resulted voids were visible in Ni deposits by high magnification SEM in Fig. 3b. A porous structure should consequently account for the continuous Ni deposition. On the contrary in a bath with no F^-, dioxide formation described by the first equation can lead to surface passivation causing self-termination of the Ni deposition [21]. Now from Fig. 3c we can see, after being immersed in the bath with F^-, neighboring sites of reaction grew to meet up with one another and merged to have had the contiguous oxide replaced by a nanoporous Ni deposits thereafter (see Fig. 3d). As a result a deposited Ni layer with interconnected voids was formed and also thickened. And long term non-limited Ni deposition was ascribed from the sponged deposits.

3.3. Si oxide as an intermediate phase during deposition

It has been found that Si oxide was generated during immersion Ni deposition. Oxidation of Si sustained Ni reduction and deposition. Oxide which played a role of intermediate phase separated Ni deposits from the Si substrates. Redox couples expressed by Eqs. (2) and (3) have been used to describe the overall processes in our Ni bath. However, the detailed oxidation and reduction can be realized by several steps; Si might be gradually oxidized from Si^0 to Si^{4+} while the released electrons kept reducing the Ni ions. Finally the fully oxidized Si (the dioxide) was etched by the fluorine ions. In the meanwhile, the reaction region was enlarged by expanding the perimeter where Si oxidation occurred to form suboxide prior to Ni deposition. To demonstrate the role of Si suboxide further, a cross-sectional TEM micrograph (see Fig. 4a) was shown at the

interfacial region. The dark colored clusters were Ni deposits. Ni deposits were surrounded by some bright material. Using a convergent electron beam in TEM, we confirmed by EDX the presence of suboxide species (Si:O ~ 48:52). It can be a combination of different suboxide types [22]. The as-formed Si oxide might not be dense resulting in Ni deposits embedded in it by further reactions. Moreover Si had experienced an anisotropic etching in the <111> direction (see Fig. 4b). That was due to NH_4F in the solution. Earlier study of etching and oxidation process on Si (100) surface revealed many (111) microfacets soon after immersion in the NH_4F solutions [23]. Fluorine ions could consume the formed Si oxide creating a porous surface layer. That might explain a continuous Ni deposition plus a continuous Si etching found in immersion Ni deposition on Si using our NH_4F containing electrolyte. Si reactions can be represented by the following indication.



$$Si \rightarrow Si^{+} + e^{-} \rightarrow Si^{2+} + e^{-} \rightarrow Si^{3+} + e^{-} \rightarrow Si^{4+} + e^{-} \quad (4)$$

$$Si^{+} + 6F^{-} \rightarrow SiF_6^{2-} + 3e^{-} \quad (5)$$

$$Si^{2+} + 6F^{-} \rightarrow SiF_6^{2-} + 2e^{-} \quad (6)$$

$$Si^{3+} + 6F^{-} \rightarrow SiF_6^{2-} + e^{-} \quad (7)$$

$$Si^{4+} + 6F^{-} \rightarrow SiF_6^{2-} \quad (8)$$

4. Conclusion

Immersion deposition of Ni on Si was studied in a simple $NiSO_4$ solution at open circuit. Addition of NH_4F to the solution enhanced the Ni nucleation in the early stage. With fluoride in the Ni bath, we observed that Ni deposits had sponge-like structure with nanopores and the inherent displacement reactions were not self-limited even after 8h immersion. During deposition, Si was gradually oxidized to release electrons for Ni reduction. The formed oxide in either a partial or a full state of oxidation could be etched away by fluorine ions and dissolved in the solution, resulting in interconnected voids which lead to a continuous immersion Ni deposition over Si.

Acknowledgement

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Figure 2. SEM micrographs of an 8-hour immersed Si sample. (a) The surface morphology of Ni deposits. (b and c) Ni deposition underneath with partial removal of the as-deposited upper layer shows no self-limiting characteristic.

Figure 3. SEM micrographs of the immersion Ni deposition progress on Si surface. (a) Initial Si oxidation and Ni reduction. (b) An enlarged reaction area with Ni deposits and Si oxide on the perimeter. (c) Meeting among the reacting regions. (d) Merging of reaction areas with the contiguous oxide being consumed

Figure 4. Cross-sectional TEM micrograph of the reaction interface. (a) Ni deposition along with Si oxidation on Si during the immersion process. (b) Oxidation of Si along (111) planes in the NH_4F containing Ni solution

Chemicals	Bath A (M)	Bath B (M)
$NiSO_4 \cdot 6H_2O$	0.1	0.1
$(NH_4)_2SO_4$	0.5	0.5
$(NH_4)F$	–	2.5

Table 1

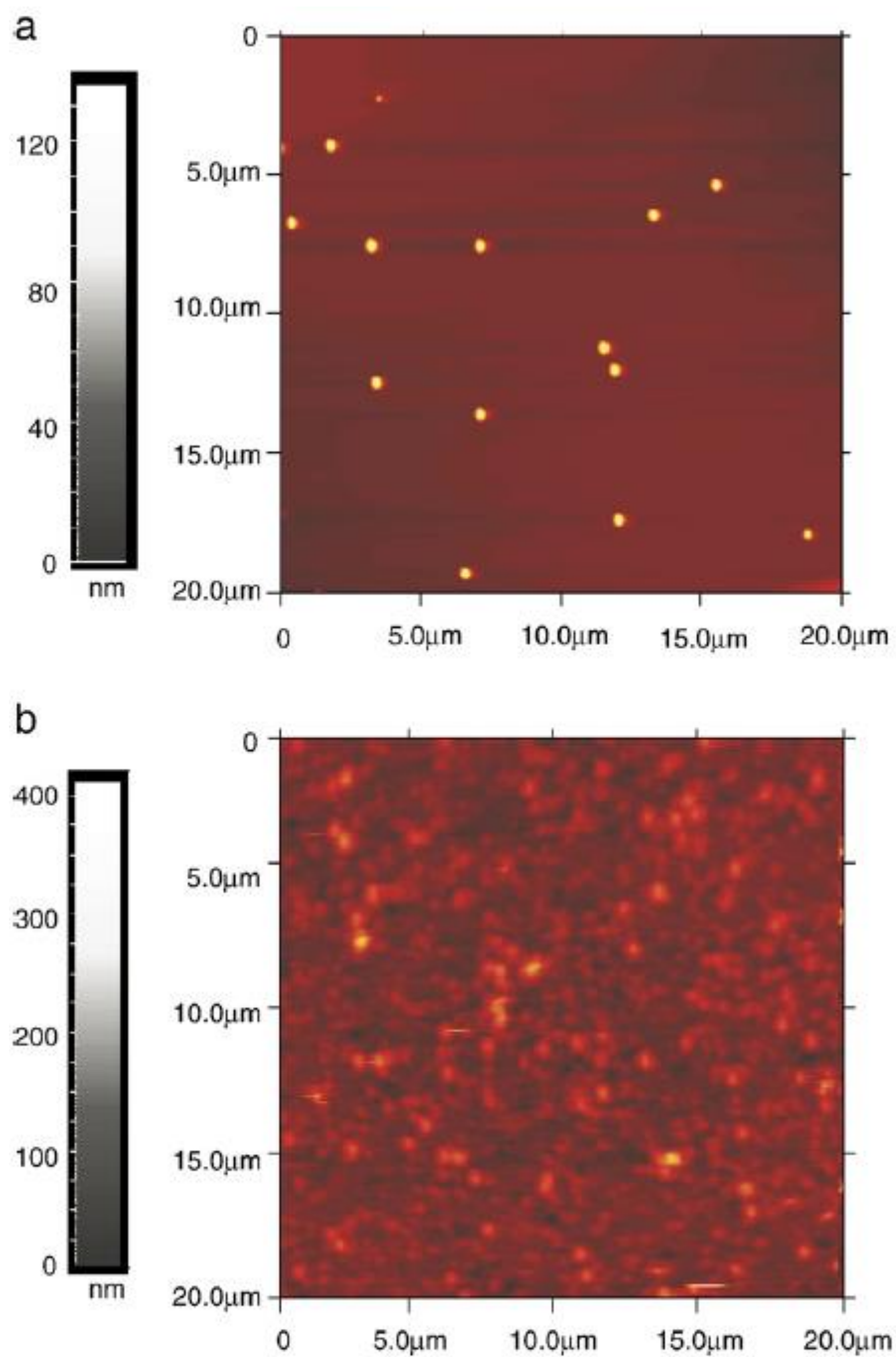
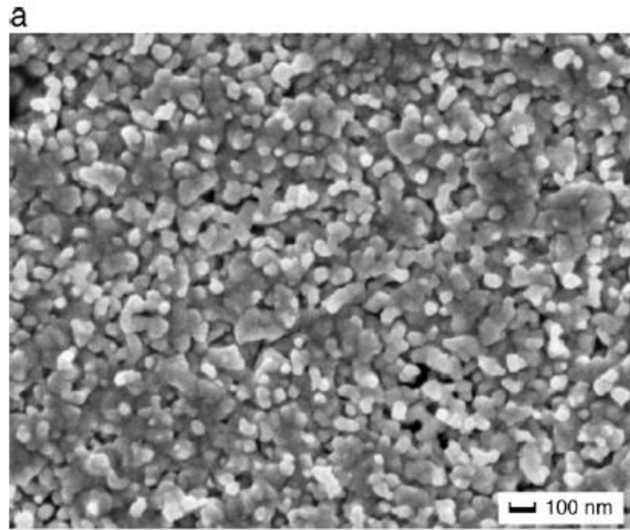
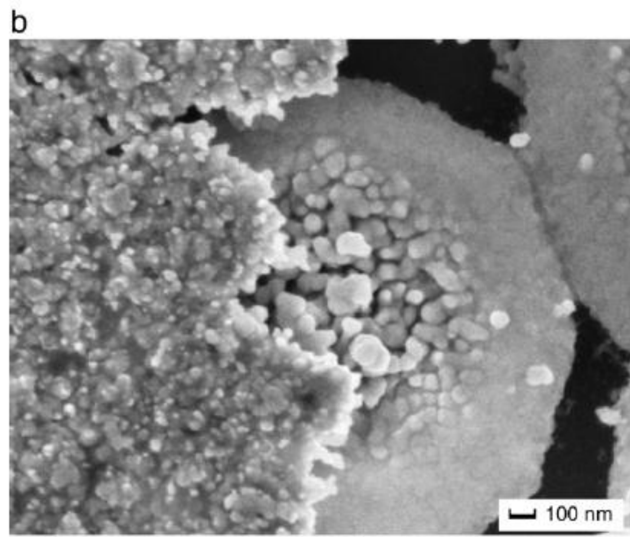


Figure 1





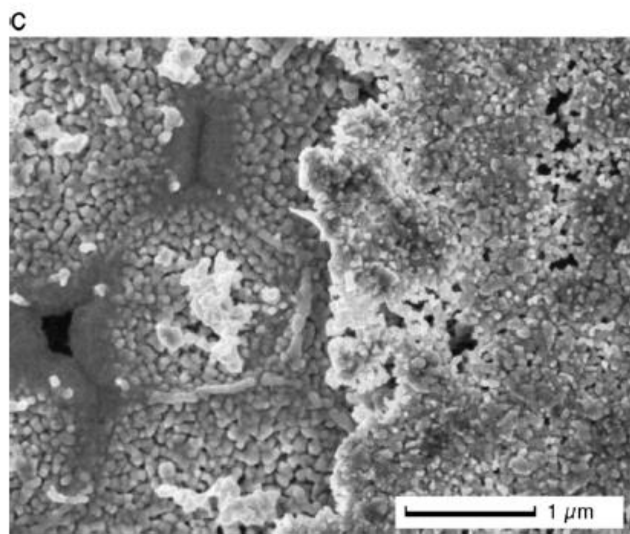


Figure 2

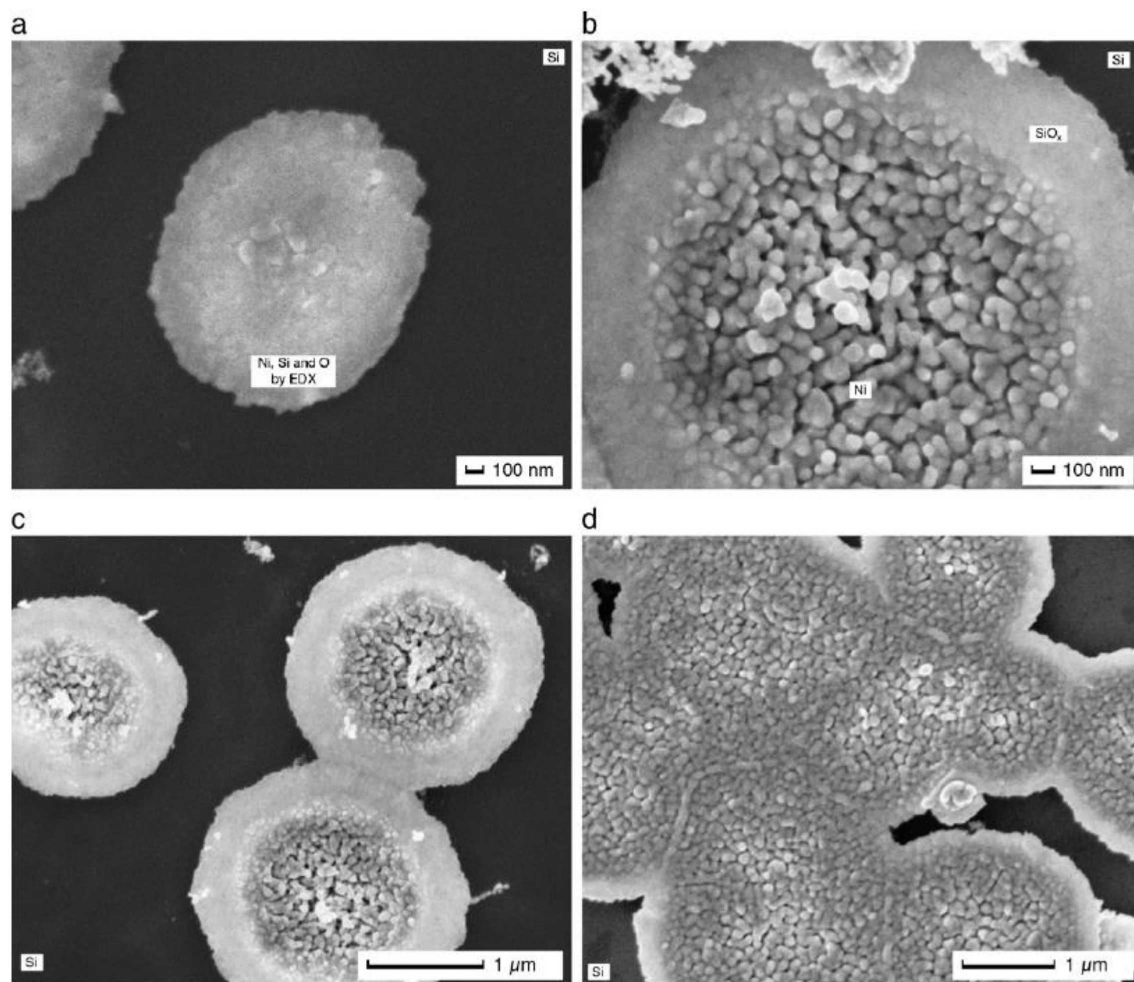
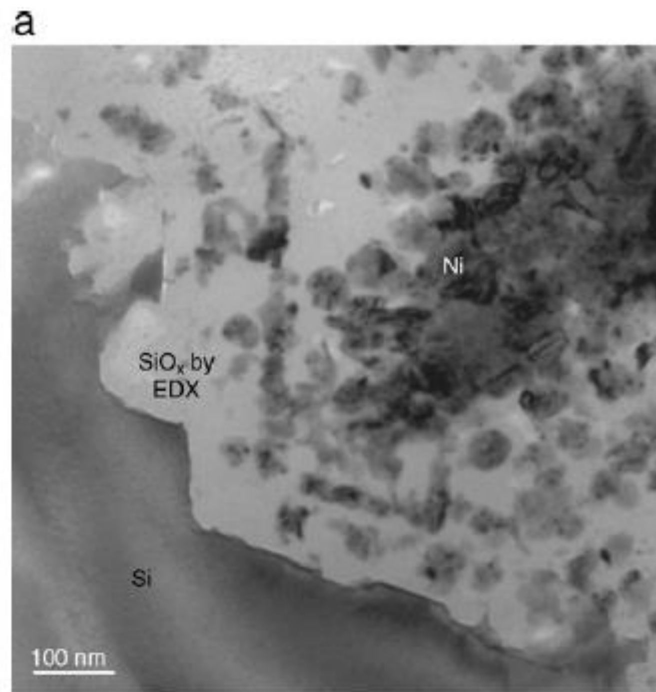


Figure 3



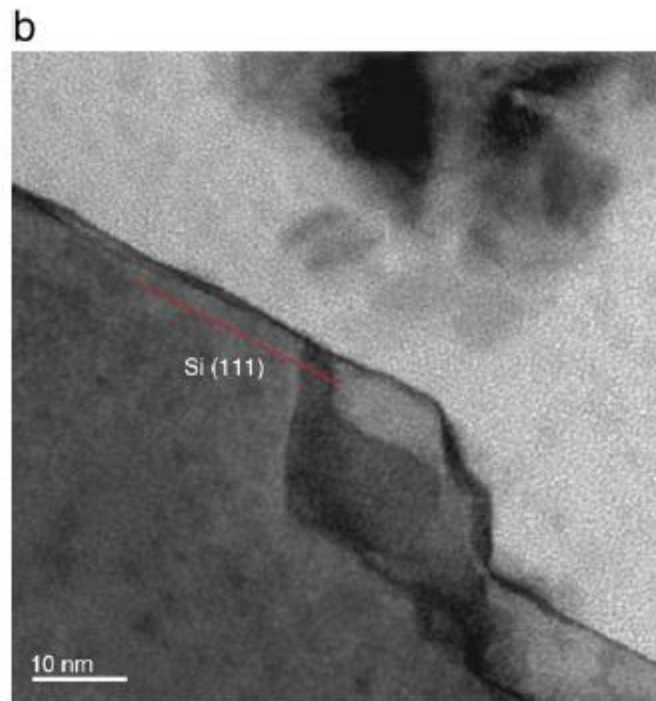


Figure 4