Study of two-step electroless etched Si nanowire arrays

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***Abstract*—The influence of the nucleation process of Ag particles on the formation of Si nanowire arrays is investigated by two-stage electroless chemical etching. The dimensions of the Ag particles formed in the first stage of the process play an important role in the formation of the Si nanowires. The nucleation and etch result are analysed using SEM. The electrical properties of the resulting Si NW arrays are also studied.**

Keywords- Si nanowire array; electroless chemical etching; Ag catalysts

I. INTRODUCTION

Silicon nanowires (NWs) have attracted much attention due to their potential application in nanoelectronics [1-5], photonics [6], energy [7-13], and biosensors [13-16]. A variety of methods, including chemical (chemical vapour deposition [14-23], chemical etching [24-30], solution growth [6] etc.) and physical (laser ablation [31] and thermal evaporation [32]) methods, have been developed to prepare high quality NWs. Of these techniques, the metal-assisted electroless chemical etching [25-30] offers the simpler and cheaper way to prepare large-area arrays with long NWs. However it is still a challenge to controllably prepare Si NWs with a uniform diameter. Properly understanding the etching mechanism would help to control the etching process and design the NW array according to the application requirements. In this paper, we apply a two-step etching technique to study the influence of Ag particles on the formation of Si NWs. We investigate the influence of the Ag nucleation on the Si surface as function of time using SEM. In addition their electrical characteristics are also investigated.

II. EXPERMENTAL

P-type Si (100) wafers with resistivity of 1-10 Ω·cm were used in our experiment. The back side of the wafer was protected by sputtering Cr/Au and can also be used as back electrode. After cleaning with acetone, isopropanol and deionized (DI) water, the samples (2 x 2 cm^2) were immersed in a solution of 0.006 M silver nitrate ($AgNO_3$) and 5.6 M HF for a short period of time for the formation of Ag particles. They were then immediately soaked into the solution of 5.6 M HF and 0.3 M H_2O_2 for 3 hours to form Si NWs. After etch, the NW array was rinsed in DI water. The residual Ag particles were removed by a highly concentrated HNO_3 (5M) solution. Contact metals, Cr/Au, were deposited on the top of the NW array by sputtering to form the other electrode. Rapid thermal annealing was applied to improve the contact characteristics.

III. RESULTS AND DISCUSSION

In order to study the effect of the nucleation of Ag particles on the surface of the Si samples on the formation of the NW array, the time of the first stage in the process – the Ag nucleation time – was varied between 10 and 65 seconds. Experiment results indicate that the Ag particles formed in the first stage play an important role in the formation of Si the NWs. A high density and uniform distribution of nano-sized Ag particles are needed to get a high density Si NW array (Fig. 1 d, e, f). The case of a low density of Ag particles covering the surface of the Si wafer is shown in Fig. 1 a. With this low density of Ag the Si wafer is not fully etched into NWs during the 2nd stage of the etch process (Fig.1 b). Only porous structures (Fig.1 c) were obtained since there were not sufficient Ag-assisted etching sites available in the etching process. Only when Ag particles covered the Si wafer surface densely as shown in Fig. 1 d, the electroless etching in the second stage, in the HF and H_2O_2 solution, can properly progress to form Si NW array structures (Fig.1 e and f). The NWs stand vertically along the [001] direction. As shown in the insets of Fig. 1 f, these NWs have a diameter of 30-200 nm. The large diameter non-uniformity could originate from the uneven Ag sizes and their random distribution on the Si surface. Due to the surface tension and electrostatic attraction, the NWs prefer attracting each other to form congregated bundles. The use of surfactants and other techniques can reduce this effect [33].

Fig. 2 shows the SEM image of the NW arrays at the cleaved edge of the wafer. Clearly, the NW arrays exhibit three different directions and they cross each other vertically. That means this electroless etching is anisotropic and the silicon is etched mainly along [00-1], [010] and [100] directions as shown in Fig. 2. The Ag particles deposited on the cleaved surface contribute to the lateral etching at the edge along [010] and [100] directions. And

this lateral etching rate is almost same as that in vertical direction according to their similar NW length.

To investigate the electrical characteristics of the array of NWs, Ohmic contacts on the medium doped p-type NW array needs to be made. Experimental results show that Cr/Au (5nm/400nm) offers the best contact with the p-type NW array. After annealing at 360 ^{o}C by rapid thermal annealing in Argon ambient for 1 min, linear current-voltage curves were obtained, see Fig. 3. A relative high resistivity of 19.5 Ω cm^2 is obtained. This value can be due to the non-continuous metal formation on the array of separated NWs (Fig. 4). This in addition to the slightly different lengths of the NWs in the array that only allow a fraction of the total number of NWs to be connected to the flat surface of the large area probe at any one time.

Another critical aspect of the contact to the top of the NW array is the penetration depth of the sputtered metal. During sputtering the Cr/Au on the top of the NW array, a 30 degree angle tilt between the wafer and metal source was applied to prevent the metal being deposited on the bottom of NWs. Energy dispersive X-ray analysis indicates that the sputtered Au can only be found on the top 10 μm of the NWs (see Fig. 5) because the NWs effectively shelter themselves.

IV. CONCLUSION

We investigated the two-step electroless chemical etching of Si NW array. The nucleation of the Ag particles plays an important role in the formation of the Si NWs. A sufficiently high density of Ag particles is needed to etch NWs in the second stage of the process, otherwise porous Si is obtained. The etching is along the <100> directions. Ar annealed sputtered Cr/Au offers the best contact with our medium p-doped NW array.

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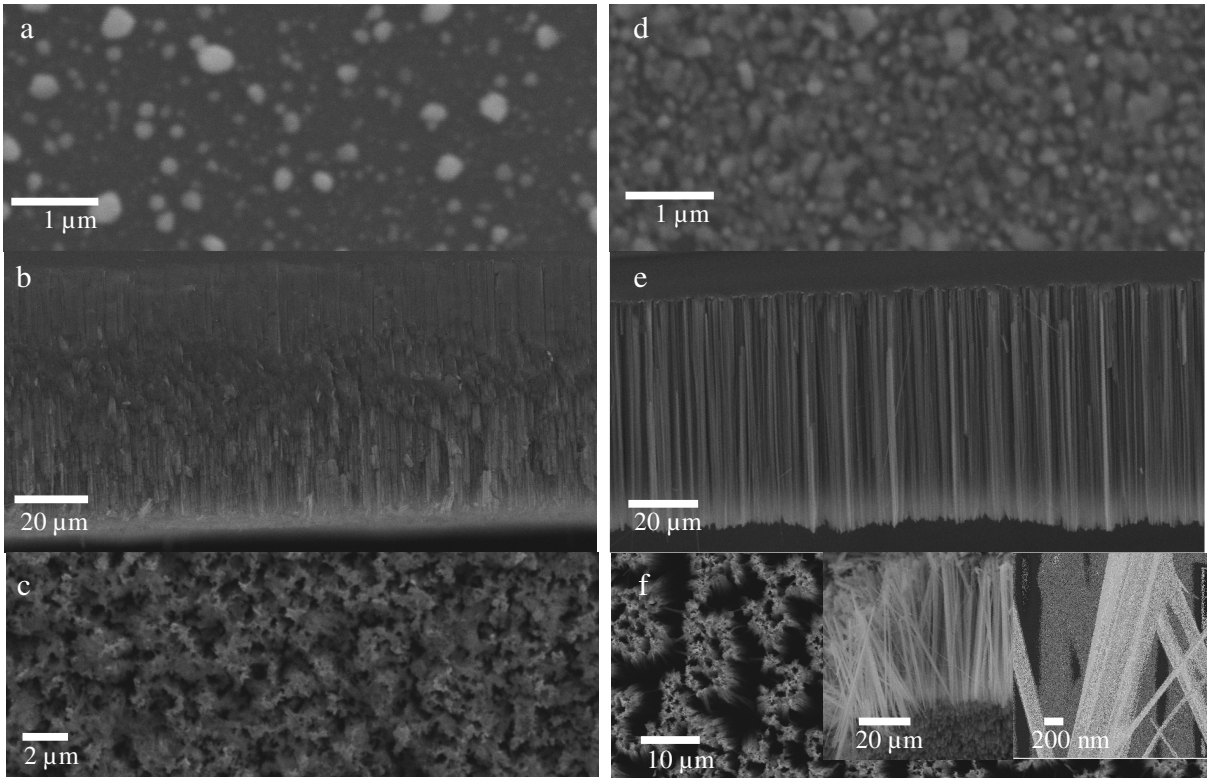

Fig. 1 a), Scanning electron microscope (SEM) image of low density Ag particles formed in the solution of 0.03 M $AgNO_3$ and 5.6 M HF for 10 seconds; Cross-section (b) and top-view (c) SEM image of the porous silicon etched from (a); d), SEM image of high density Ag particles formed in the solution of 0.03 M $AgNO_3$ and 5.6 M HF for 65 seconds; Cross-section (e) and top-view (f) SEM image of the silicon NW array etched from (d). The insets in (f) show the high magnification SEM images of the NWs.

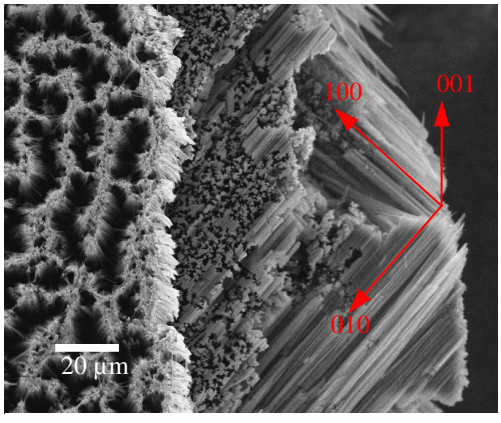

Fig. 2, SEM image of the NW arrays etched at the cleaved edge of the wafer.

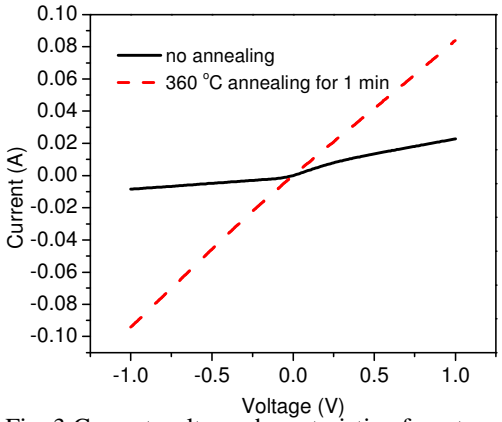

Fig. 3 Current-voltage characteristic of a p-type NW array with Cr/Au as top and bottom contacts. Contacts become Ohmic after anneal at 360 °C for 1 min.

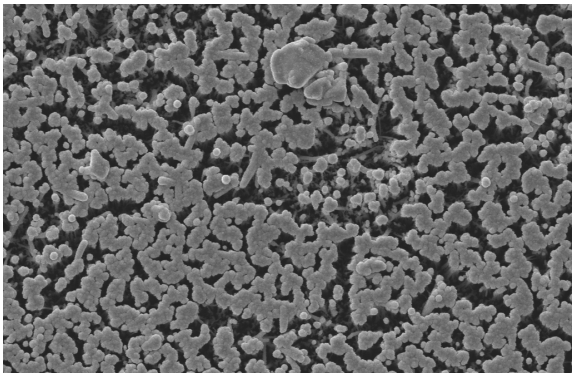

Fig.4 SEM picture of the top of the metallised Si NW array

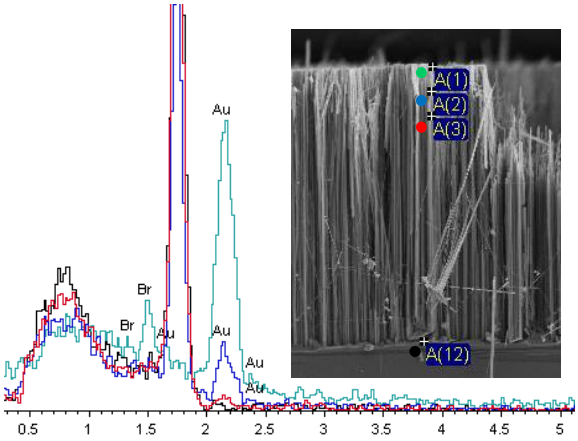

Fig. 5 Energy dispersive X-ray analysis along the cross section of the NW array. The X-ray was spotted at the dotted area shown in the inset. The Au can only be found on the top 10 µm of the NWs.