

# A novel method for realization of nickel silicide nanosheets with advanced morphology and photoemission

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## ABSTRACT

Morphologically controlled nanostructures have been increasingly important because of their strongly shape dependent physical and chemical properties. Formation of nanoscale silicon based structures that employ high levels of strain, intentional, and unintentional twins or grain boundaries can be dramatically different from the commonly conceived bulk processes. We report, realization of highly crystallographic 3D nanosheets with unique morphology and ultra-thin thickness by a stress-induced oriented-diffusion method, based on plasma processing of metal layer deposited on Si substrate and its post deep reactive ion etching. Annealing in plasma ambient creates rod-like metal alloy precursors which induce stress at its interface with Si substrate due to the mismatch of lattice constants. This stress opens facilitated gateways for orientated-diffusion of metal atoms in  $\langle 110 \rangle$  directions and leads to formation of NSs with [111] crystalline essence. Nanosheets are mainly triangular, hexagonal or pseudo hexagonal in shape and their thicknesses are well controlled from several to tens of nanometers.

**Keywords:** Morphologically controlled, oriented-diffusion, nanosheet, plasma processing.

## 1 INTRODUCTION

Synthesis of morphologically controlled nanomaterials are mostly limited to some solution based methods. The atomic arrangement of nanomaterials constituting components, during evolutionary stage, determines their morphology that intensely influences their physical and chemical characteristics [1-5]. Therefore, morphologically controlled methods are appealing for applications demand different shape of nanomaterials with the same route [6-7]. Transition metal/-silicides are one of the main target of morphologically controlled techniques, due to the prospecting features of these types of materials [8-9]. There are some reports on synthesis of one-, two-, and three-dimensional nanostructures of such materials which mainly employ reduction of metals agents by solution based techniques [8-9]. Although crystalline quality of synthesized nanostructures by these techniques, in the solution environment, are acceptable but their assembling on the desired substrate leads to introduction of significant

stress/strain and reduces their functionality. In addition, every wet-chemical method specifically can be used for realization of a particular type of nanomaterial and also is incompatibility with the existing CMOS technology. The mentioned drawbacks expose necessity of more reliable general technique applicable for fabrication of wide range of transition metal/-silicide in line with the industrial requirements. Nickel silicide as a member of transition metal silicides has appealing properties such as narrow bandgap, low electrical resistivity and high resistance to oxidation, corrosion and etching [10-12]. It is one of the promising materials in the critical utilization for the future low-dimensional nanoelectronics [13-14] and also can be used as a promising intermediate for silicide sheets evolution [15]. During the last decades, only 1D nickel silicides nanostructures are studied and a little is known about its 2D and 3D counterparts [16-17]. Most of studies on silicides have been concentrated on kinetics of reaction and phase identification [10-12], however, very little is known about the causes of observed structural and morphological features of such materials. Thus, investigation on the properties of the morphology-controlled nanostructures with particular size, shape and especially with specific exposed surfaces is necessary.

Here we report a novel generic method applicable for realization of wide spectrum of nano materials. The proposed method is a stress-induced oriented-diffusion process which has been developed for the first time and highly crystallographic three-dimensional nickel silicide nanosheets with controlled-morphology were obtained by this process. It is shown that by thermal annealing accompanied with a specific plasma treatment, rod-like nickel precursors on the surface of Si substrate form which leads to gateways formation due to mismatch of lattice constants at its interface with substrate. Orientated diffusion of nickel atoms between neighboring (111) planes in  $\langle 110 \rangle$  directions is expedited through these gateways. It is just like unzipping silicon from certain places and inserting nickel atoms in those linear regions. NSs are mainly triangular, hexagonal or pseudo hexagonal in shape and are arranged in a definite orientation with respect to each other. The obtained NSs have preferentially (111) planes orientation and the opposite edges of all the sheets are parallel with one another. To the best of our knowledge, this is the first report on the three-dimensional formation of nickel silicide NSs with such morphology and properties as the direct result of

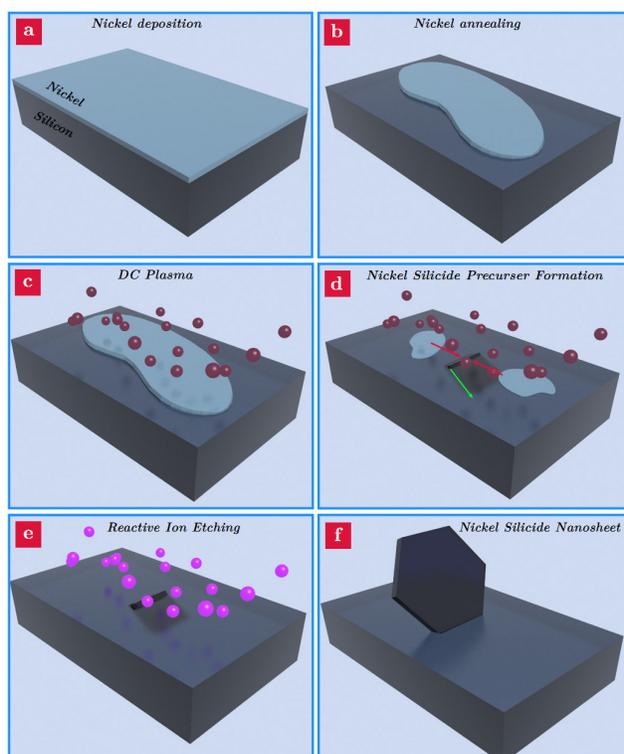
innovative sheets development process. These ultra-thin nanosheets show noticeable photoluminescence (PL) at different wavelengths as the consequence of quantum confinement effects in their very fine structure. We expect that this approach will open up new opportunities towards facile and controllable development of NSs of other transition metals/-silicide. Furthermore, by mediating such crystalline nickel silicide nanosheets and applying metal-induced growth method, three-dimensional crystalline Silicin films can be acquired.

## 2 FABRICATION PROCESS

The process of nickel-silicide NSs formation is composed of some major consecutive steps (figure1). First silicon samples which are coated with a 2nm layer of nickel, placed in a DC plasma reactor and then nickel and silicon thermally react at temperature of 650°C in H<sub>2</sub> atmosphere. This reaction leads to partial formation of nickel silicide islands. By introducing H<sub>2</sub> or N<sub>2</sub> gases to the reaction chamber and in presence of DC plasma, horizontal rod-like nickel silicide precursors form on the surface of silicon substrate. These precursors induce stress to the underlying substrate due to lattice mismatch between nickel silicide and silicon substrate and lead to the formation of line defects. Then oriented diffusion of nickel between (111) planes in a <110> directions occurs through the formed gateways. Afterwards, exploiting a reactive ion etching on the prepared samples, the silicon atoms surrounding covered nickel-silicide sheet are etched away which in term nickel silicide are exposed.

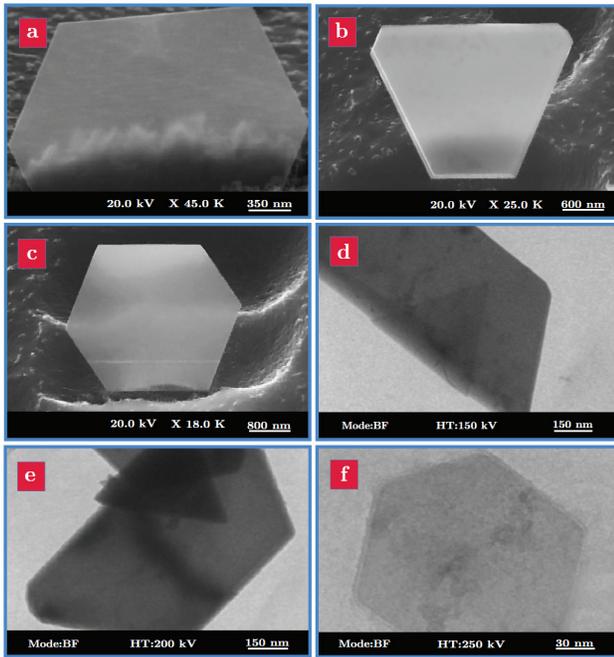
## 3 RESULTS AND DISCUSSION

Morphological characteristics of these nanosheets were investigated thoroughly by scanning electron microscope (SEM), transmission electron microscope (TEM) and atomic force microscope (AFM), because precise understanding of morphology of the NSs is closely related to their active properties. The SEM and TEM micrographs of nickel-silicide NSs are depicted in Figure 2 and 3. As seen, the NSs are mainly triangular, hexagonal and pseudo hexagonal in shapes which are semi-transparent on SEM views due to their ultra-thin thickness. The measured diffusion angles of NSs are close to the angle between {111} and {100} planes (54.7°) (figure 4). In addition, a measured angle between adjacent sides of the NSs are 60° and 120° which are the angle between <110> planes (figure 4). As it is deduced from orientation relations, the nickel silicide nanosheets preferentially have the (111) crystal plane orientation and diffuse in <110> directions (Figure 2(e)-2.(g)). The preferred diffusion along the <110> directions can be arisen from the minimization of the total surface energy as a result of (111) planes appearance.

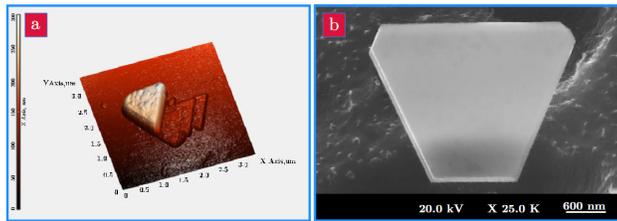


**Figure 1:** Schematic of NSs in their different evolutionary stages. (a) Nickel coated silicon substrate, (b) Nickel island formation by thermal process, (c) DC-plasma processing, (d) Nickel rod-like precursor formation and defect gateways creation. (e) Reactive ion etching of pre-processed samples to excavate NSs from the substrate. (f) Excavated 3D NSs.

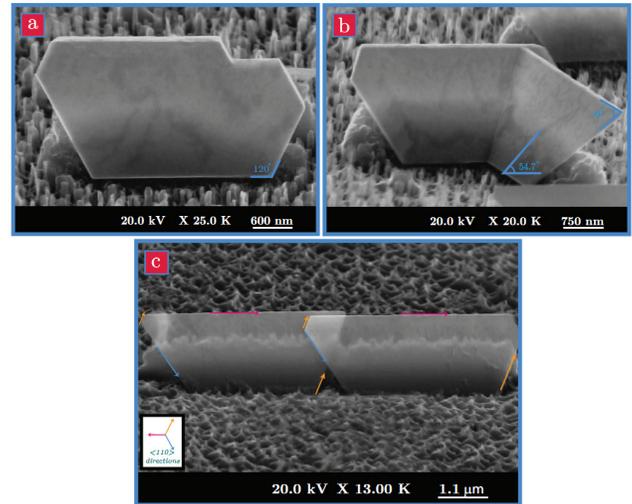
These ultra-thin NSs show unique optical properties of photo luminescence (PL) that would be ascribed to the enhanced direct band gap. The preferential adsorption of nickel silicide atoms along the (111)-type plane could be responsible for the formation of ultrathin NSs. It was reported that 2D nanostructures are under compressive strain due to surface tension [26] and the compressive strain can influence direct band gap transition in NSs. The compressive stress in the NSs could be attributed to the three dimensional topography, ultra-thin thickness and also the volume changes at the silicide interface due to the reaction of Ni and Si. The PL spectrum exhibited the broad peaks with maximum intensity around wavelengths of 339, 367, 440, 520 and 534nm (figure 5).



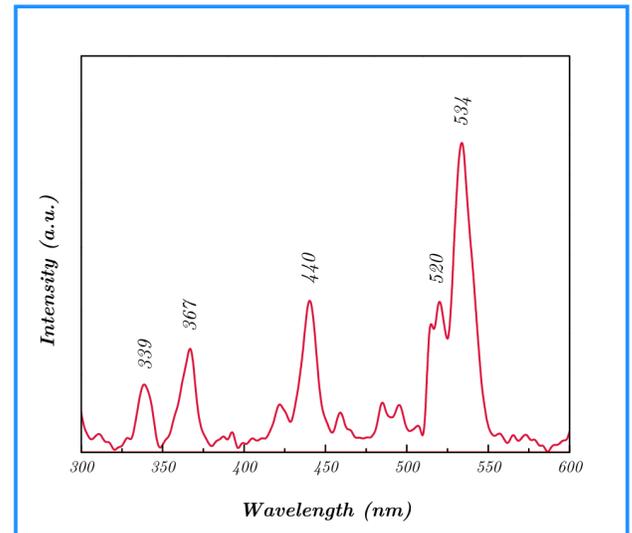
**Figure 2:** SEM and TEM micrographs of nickel silicide NSs. The nanosheets are mainly triangular, hexagonal or pseudo hexagonal in shape.



**Figure 3:** AFM and SEM micrograph of NSs with triangular morphology.



**Figure 4:** SEM images of the Nickel silicide NSs. The nanosheets have a definite orientation with one another. The measured diffusion angles of NSs are close to the angles between  $\{111\}$  and  $\{100\}$  planes ( $54.7^\circ$ ). Measured angle between adjacent sides of the NSs are  $60^\circ$  and  $120^\circ$  which are the angle between  $\langle 110 \rangle$  planes. Opposite edges of all NSs which are in a same plane are parallel with each other that are parallel to the three arrows, separately.



**Figure 5:** PL spectrum of nickel silicide NSs. Photo luminescence spectrum of the NSs exhibited broad peaks with maximum intensity around wavelengths of 339, 367, 440, 520 and 534nm due to quantum confinement effects in ultra-thin NSs.

## 4 CONCLUSION

In summary, the present study reports a stress-induced oriented-diffusion method for realization of highly crystallographic 3D nickel silicide nanosheets with unique morphology and ultra-thin thickness based on the reaction of nickel layer on Si substrate in plasma environment and its post deep reactive ion etching (DRIE). The NSs formed through the orientated diffusion of nickel atoms between neighboring (111). The plasma was found to be a critical factor in the formation of these NSs. The orientation relation between nanosheets and texture like patterns on them are investigated which confirms the formation mechanism. This material with such high intensity PL peaks can be used for future silicon-based optical devices. We believe that, this approach is applicable to other transition metal silicides. Moreover, the formation of highly crystalline films could end up with the formation of silicine-like layers. Also this work can introduce a new physics into metal diffusion into crystalline structures.

## REFERENCES

- [1] a Courty, A.-I. Henry, N. Goubet, and M.-P. Pileni, *Nature materials*, vol. 6, no. 11, pp. 900–7, Nov. 2007.
- [2] L. Yin . Y. Bando, *Nature materials*, vol. 4, no. December, pp. 883–884, 2005.
- [3] R. Jin, Y. C. Cao, E. Hao, G. S. Me, G. C. Schatz, and C. A. Mirkin, *letters to nature*, no. 4, pp. 487–490, 2004.
- [4] S. E. Habas, H. Lee, V. Radmilovic, G. a Somorjai, and P. Yang, *Nature materials*, vol. 6, no. 9, pp. 692–7, Sep. 2007.
- [5] W. a El-Said, H.-Y. Cho, C.-H. Yea, and J.-W. Choi, *Advanced materials*, pp. 910–918, Dec. 2013.
- [6] M. Chen, B. Wu, J. Yang, and N. Zheng, *Advanced materials*, vol. 24, no. 7, pp. 862–79, Feb. 2012.
- [7] T. K. Sau and A. L. Rogach, *Advanced materials*, vol. 22, no. 16, pp. 1781–804, Apr. 2010.
- [8] C. Lofton and W. Sigmund, *Advanced Functional Materials*, vol. 15, no. 7, pp. 1197–1208, Jul. 2005.
- [9] L. Lu, X. Yan, J. Wang, H. Zheng, X. Hu, Y. Tang, and Z. Jia, *The Journal of Physical Chemistry C*, vol. 116, no. 27, pp. 14638–14643, Jul. 2012.
- [10] A. L. Schmitt, J. M. Higgins, J. R. Szczech, and S. Jin, *Journal of Materials Chemistry*, vol. 20, no. 2, p. 223, 2010.
- [11] W.-L. Chiu, C.-H. Chiu, J.-Y. Chen, C.-W. Huang, Y.-T. Huang, K.-C. Lu, C.-L. Hsin, P.-H. Yeh, and W.-W. Wu, *Nanoscale research letters*, vol. 8, no. 1, p. 290, Jan. 2013.
- [12] K. De Keyser, C. Van Bockstael, R. L. Van Meirhaeghe, C. Detavernier, E. Verleysen, H. Bender, W. Vandervorst, J. Jordan-Sweet, and C.

- Lavoie, *Applied Physics Letters*, vol. 96, no. 17, p. 173503, 2010.
- [13] F. Léonard and a A. Talin, *Nature nanotechnology*, vol. 6, no. 12, pp. 773–83, Dec. 2011.
- [14] W. W. Wu, K. C. Lu, K. N. Chen, P. H. Yeh, C. W. Wang, Y. C. Lin, and Y. Huang, *Applied Physics Letters*, vol. 97, no. 20, p. 203110, 2010.
- [15] J. Kim, C.-S. Han, Y. C. Park, and W. a. Anderson, *Applied Physics Letters*, vol. 92, no. 4, p. 043501, 2008.
- [16] C. a. Decker, R. Solanki, J. L. Freeouf, J. R. Carruthers, and D. R. Evans, *Applied Physics Letters*, vol. 84, no. 8, p. 1389, 2004.
- [17] Y. Chen, Y.-C. Lin, X. Zhong, H.-C. Cheng, X. Duan, and Y. Huang, *Nano letters*, vol. 13, no. 8, pp. 3703–8, Aug. 2013.