Surface Integration Effect on Mechanical and Piezoelectric Properties of ZnO Nanorods

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Abstract

This study is based on the effect of surface integration on the piezoelectric and mechanical properties of Zinc oxide (ZnO) nanorods. To verify that surface integration effect exists for both soft and hard substrates, Graphene coated pet plastic substrates and silver coated glass substrates were used for the synthesis of ZnO nanorods. Few sample surfaces were integrated with ZnO nanoparticles before the growth while others were used without dispersion of ZnO nanoparticles. Acquired results revealed the divergence in growth densities of nanorods on both soft and hard substrates. A clear influence of surface integration was observed in the generated piezoelectric potential in both cases. Beside this mechanical stability of seed assisted ZnO nanorods was higher than the ZnO nanorods grown on nonintegrated substrate. This approach can help the research community in future for fabrication of high quality devices on soft and hard substrates as far as mechanical stability and piezoelectric properties are concerned.

Key Words: Surface integration effect, ZnO nanorods, Soft and hard substrates, Mechanical and Piezoelectric properties

Introduction

Many researchers in past worked hard on the mechanical properties in order to enhance the amount of harvesting piezoelectric potential from different materials. Various methodologies have been utilized so far to obtain the largest amount of potential. ZnO is one of the most promising material utilized for this application with different morphologies for harvesting piezoelectric potential through various techniques like electromechanical coupling, vibration, wind, and thermal, etc. [1-5] Also, different p-types polymers have also been used along with ZnO for harvesting piezoelectricity. Similarly, different substrates have been tried for such application for analysis of the generated amount of piezoelectricity. Wang et al has been working for many years by using various methods for harvesting as much as possible amount of potential through the different environment friendly approaches. Willander et al. has also been working on the generation of piezoelectric potential from different conventional substrate along with different non-conventional resources like high flexible plastic as substrate, common paper substrate and also textile for personal electronics. Wang et al presented a mathematical model for harvesting piezoelectric potential from ZnO nanorods/ nanowires though the electromechanical coupling or by the influence of external forces/ load [6-10]. Riaz et al. has also utilized Si as a substrate for growing the ZnO nanorods/wires for the generation of piezoelectric potential. Yousuf et al. has performed the similar work on paper substrate. Khan et al. has also been doing this kind of approach for the smart electronics and presented the textile based nanogenerator for harvesting piezoelectric potential from ZnO nanorods/ nanoneedles/ nanoflowers. Kamran et al. has also presented an idea for generation of the amount of potential from hand writing based electric circuit. Mushtaque et al. has used Aluminum foil for harvesting piezoelectric potential. A ZnO and carbon nanotubes based nanogenerator has also been used for harvesting piezoelectricity in the past few years [11-15].

In present effort ZnO nanorods were grown on graphene coated plastic substrate with and without deposition of seed layer on two different substrates. The amount of piezoelectric potential generated from ZnO nanorods on integrated (seeded) surface was higher than in magnitude on nonintegrated (unseeded) substrate. For comparison, similar investigation was performed on silver coated glass substrates with and without nanoparticles deposition.

Experimental Procedure

Initially two samples were prepared for the analysis of surface integration on the piezoelectric properties of ZnO nanorods. First sample was prepared by the seed free synthesis of ZnO nanorods, while another sample was prepared after surface integration of the substrate by using the ZnO nanoparticles for synthesis of ZnO nanorods. Similarly, two more samples were prepared on silver coated glass substrate for comparison.

Seed Free Growth

The growth of ZnO nanorods was performed by using aqueous chemical growth methods without seed particles. Initially, the samples (one sample of graphene coated PET polymer and other of silver coated glass) were cleaned with the necessary chemicals like acetone and isopropanol to avoid the doping of unwanted particles. Aqueous solution with 0.75 M was prepared for the synthesis of ZnO nanorods by dissolving zinc nitrate hexahydrate ($ZnN_2O_6 . 6H_2O$) in 200 ml deionized water via magnetic stirrer. During stirring ammonia (25%) solution was added drop wise to reach the pH of solution about nine at room temperature. Then the samples were attached to the sample holder and dipped into the prepared aqueous solution. Later this container covered by aluminum foil, placed into the oven for 6 hours at a temperature of 90ºC [16].

Seeded Growth

A similar procedure was used for the synthesis of ZnO nanorods as used for the seed free synthesis, here ZnO nanoparticles were used for the synthesis of ZnO nanorods on graphene coated PET polymer and silver coated glass substrate. The spin coater was used for the application of seed layer on the surface of substrates at the speed of 4000 r.p.m, this process was repeated three times to have a good and a homogeneous layer of seed particles on the surface of substrates. After seeds layer, the substrates were heated at a temperature of 80ºC for half an hour to have a good sticking of seeds on the surface. Now then the samples were attached to the sample holder and dipped into the already prepared aqueous solution of pH 9, placed into the oven for growth of ZnO nanorods as earlier. After synthesis time all samples were put out and cleaned with deionized water and dried with nitrogen for further characterization [17].

Results and Discussion

Fig. 1 showing the SEM images of ZnO nanorods grown on graphene coated plastic substrate (a) non-integrated surface and (b) integrated surface with seeds. Similarly, the growth of ZnO nanorods on silver coated glass substrate (c) non-seeded and (d) seeded substrate. The growth images of ZnO nanorods in Fig. 1 (a) and (b) clearly indicates the difference in growth densities of nanorods on both surfaces. Non-integrated (plane) sample surface shows less growth density as compared to the growth of ZnO nanorods on the integrated surface [18]. Also, nanorods were grown on seeded substrate are more aligned and highly oriented in c-axis direction. But the nanorods on unseeded sample were not properly oriented in c-axis direction [19]. A similar trend of growth was observed on silver coated glass substrates shown in Fig. 1 (c) and (d) as on Fig. 1 (a) and (b).

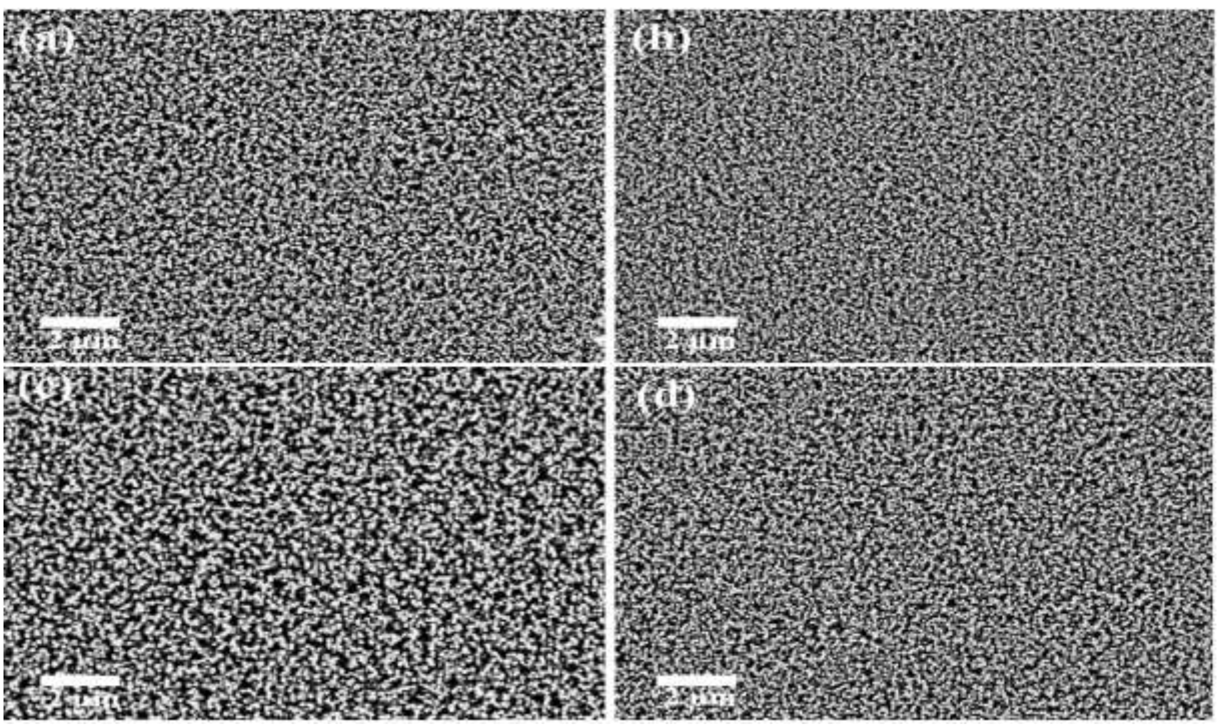

Fig. 1 *SEM image of ZnO nanorods grown on PET polymer substrate (a) without seed solution, (b) surface integration with seed solution, silver coated glass substrate (c) without seeds, (d) with seeds solution.*

In Fig. 2 (a), red and black color graphs associated with the two different samples. Although both graphs are similar but minor changes have been observed in the intensities of different peaks. Those peaks, which are most common and associated to the ZnO are present in the XRD pattern of the grown ZnO nanorods on a Graphene coated plastic substrate with seeds and without seeds. It is also seen that, in both XRD patterns the peaks associated with the z-axis are more intense than the other peaks. This high intensity of ZnO nanorods along (002) direction is indicating the grown orientation of nanorods as are vertically well aligned. Similarly, two samples were prepared on a silver coated glass substrate with seeding and without seeding. Fig. 2 (b) showing their outputs, which indicates the same growth pattern and similar alignment of ZnO nanorods in c-axis direction [18-19].

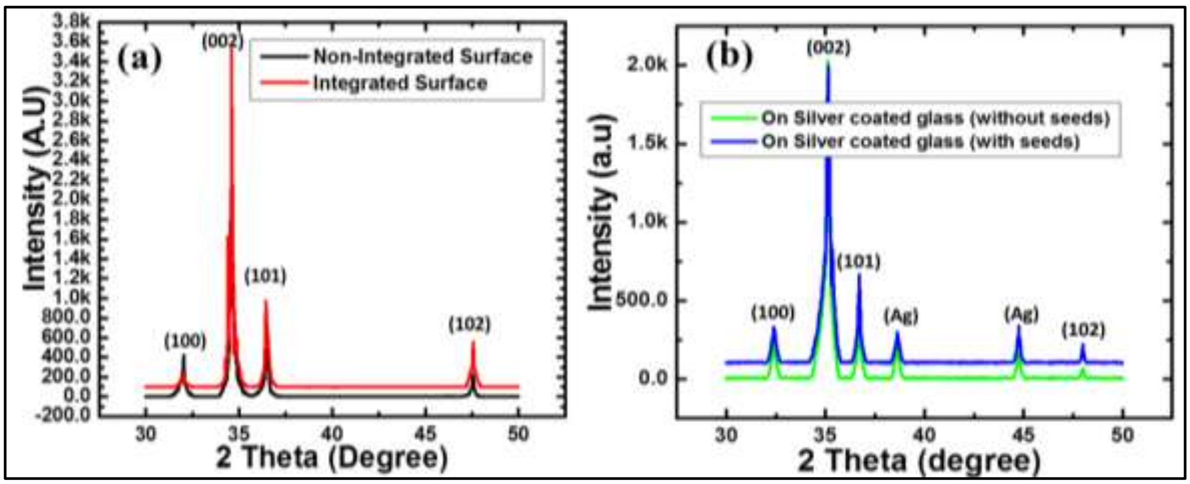

Fig. 2 *XRD of ZnO nanorods grown on graphene coated plastic substrate without seed particles (Black) and integrated with seed particles (Red), on silver coated glass substrate without seed (Green) and with seed (Blue).*

Fig. 3 is showing the growth densities of ZnO nanorods as a function of area. Trend in the graphs of growth densities clearly show the growth domination on integrated surfaces as compare to non-integrated surfaces. In Fig. 3(a) black curve is showing the amount of nanorods with respect to area for unseeded substrate and red curve is indicating the amount of nanorods with respect to area for integrated substrate. It is evident from both curves that integrated substrate has high density of nanorods then non-integrated surface [19]. Identical kind of behavior was also recorded for silver coated glass substrate as showed in Fig. 3 (b).

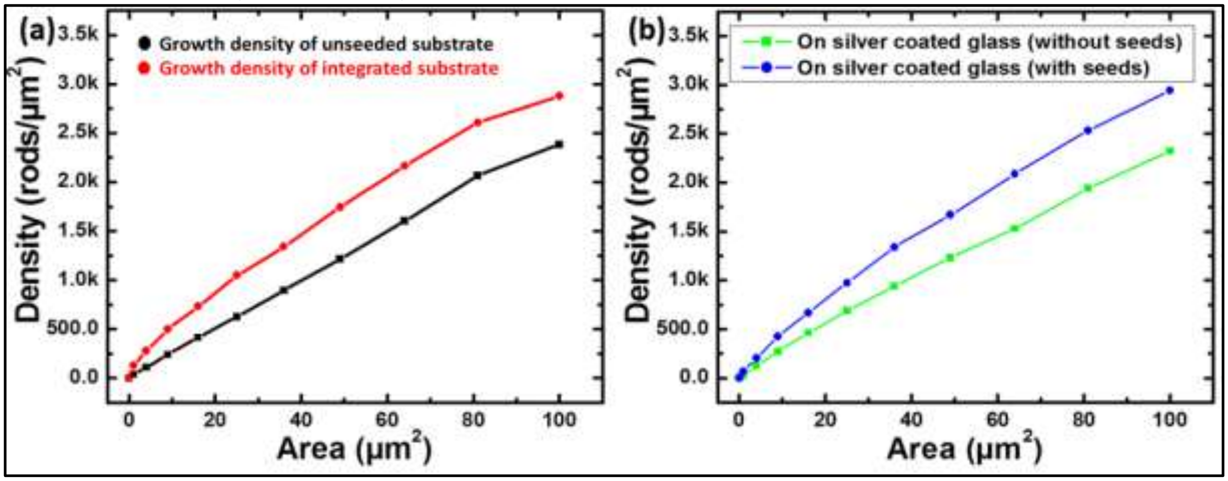

Fig. 3 *Growth density of ZnO nanorods grown (a) on graphene coated plastic substrate without seed particle (Black) and integrated with seed particles (Red), (b) on silver coated glass substrate without seed (Green) and with seed (Blue).*

The force of 20 μN was applied vertically on the grown ZnO nanorods to measure the compression angle as a function of applied force. Fig. 4(a) indicates that the compression angle is increasing with increases in applied force. ZnO nanorods on non-integrated surface attain zero degree while on integrated surface nanorods rods attain 20 degree. This shows that the mechanical stability of ZnO nanorods on integrated surface is more reliable than the non-integrated surface. This kind of behavior may be seen in the Fig. 4 (b) for silver coated glass substrate [20-21].

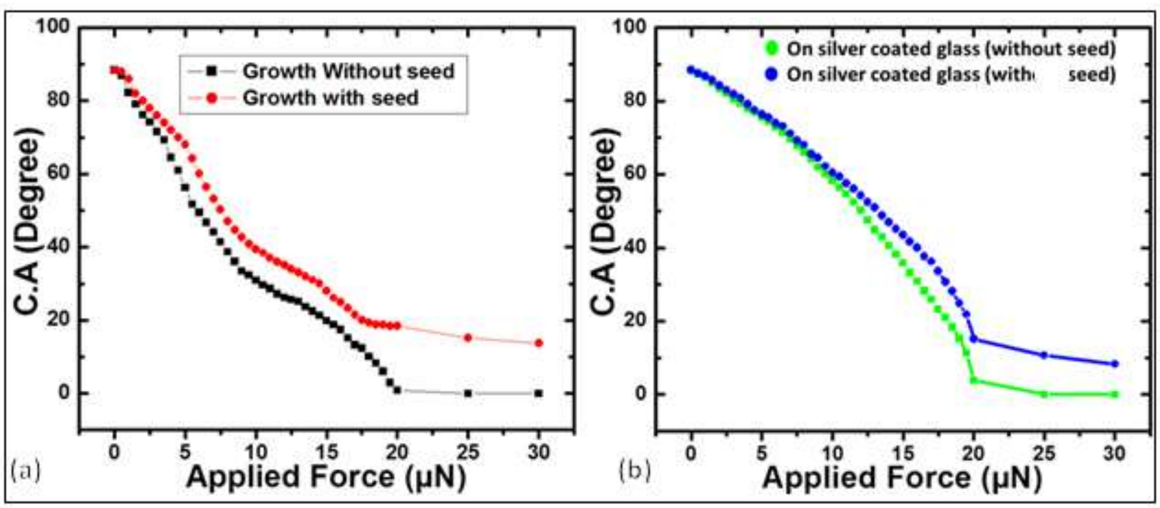

Fig. 4 *Compression angle as a function of applied force on (a) graphene coated plastic substrate without seed (Black) and integrated with seed particles (Red), (b) silver coated glass substrate without seed (Green) and with seed (Blue).*

Fig. 5 is describing the relation between force and displacement. At the surface of non-integrated graphene coated plastic substrate the maximum displacement was 186.3 nm and the displacement after indentation was 113 nm and the elastic recovery was 40.5% as shown in Fig.

5(a), while at the integrated surface of graphene coated plastic substrate the maximum displacement was 685.2 nm and the displacement after indentation was 255.3 nm and the elastic recovery was 62.8% which can be seen in Fig. 5 (b). The comparison between both figures examine that the mechanical stability of ZnO nanorods on integrated surface is more than the non-integrated surface. Also the elastic recovery confirm that the integrated ZnO nanorods have much better mechanical properties as compare to non-integrated substrate. Moreover, for confirmation of the mechanical properties a similar reproduction was taking into account on silver coated integrated glass substrate and non-integrated substrate. This may also observe in Fig. 5 (c) and (d) the mechanical properties of ZnO nanorods grown on integrated substrate were better as compare to the non-integrated substrate. The elastic recovery of the ZnO nanorods on integrated surface was found to be 67.2% and the elastic recovery of ZnO nanorods on non-integrated substrate was 33.5%, which is almost half in magnitude as compare to integrated surface [22-25].

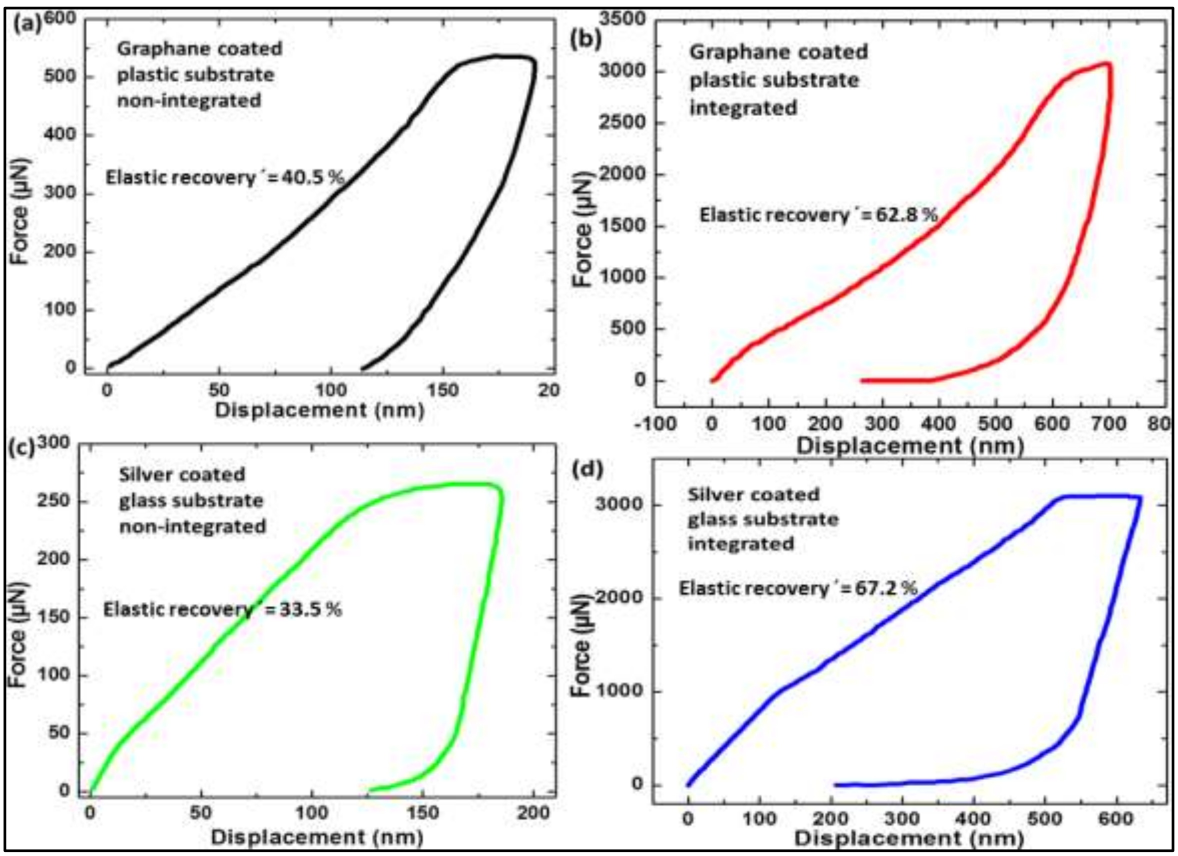

Fig. 5 *Applied force as a function of displacement (a) Graphene coated plastic substrate without seeds (Black) and (b) with seeds (Red), (c) silver coated glass substrate without seeds (Green) and (d) with seeds (Blue).*

In Fig. 6(a) the generated current was recorded by digital atomic force microscopy and displayed in terms of 2D and 3D pulses of piezoelectric potential. When the tip scan vertically well aligned ZnO nanorods then compression taking into account in the nanorods, due to the electromechanical coupling of the nanorods [26]. Fig. 6(a) is displaying the sharp pulses of piezoelectric potential in 3D associated to the ZnO nanorods grown on non-integrated plastic substrate with magnitude of more than 6 mV, while in Fig. 6 (b) nanorods were grown with seeds showing more intense peaks with generated piezoelectric potential of magnitude more than 14 mV. A similar measurement was performed on silver coated glass substrate without seeds and with seeds as shown in Fig. 6 (c) and (d). The amount of piezoelectric potential from non-seeded surface was 5 mV while on integrated surface was 9 mV. The captured results of generated piezoelectric potential reveals the importance of seeds integration and shows that the integrated substrate can affect the performance of device, which may leads to enhance the overall properties of device [27].

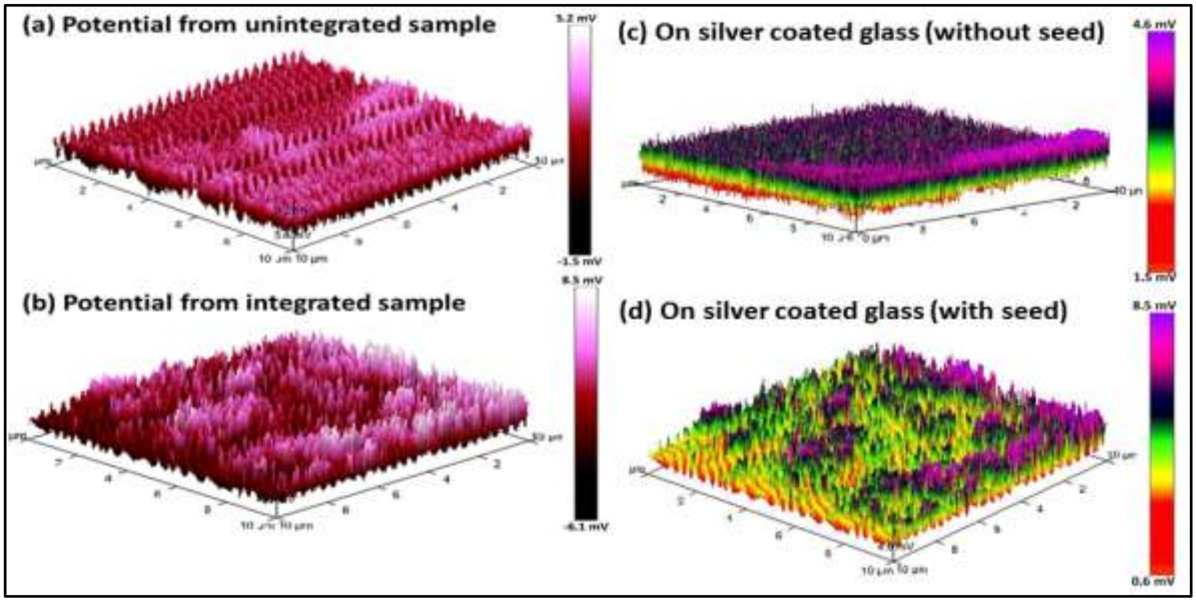

Fig. 6 *3D pulses of generating piezoelectric potential from ZnO nanorods grown on (a-b) graphene coated plastic substrate (c-d) silver coated glass substrate.*

Fig. 7 is revealing the line profile generated piezoelectric potential via AFM tip scanning in a small area of (10µmX10µm) in 2D. In Fig. 7 (a), two different color line profiles are associated to the piezoelectric potential from the non-integrated (Black) surface and integrated surface of pet polymer surfaces (Red). This may see clearly in the picture that, magnitude of generated output potential from integrated surface is more as compare to non-integrated surface. This shows the mechanical stability and high recovery of ZnO nanorods grown on integrated surface. Similarly, in Fig. 7 (b), similar results have observed on glass substrates. The amount of output potential from ZnO nanorods grown on integrated surface (Blue) is more than in amount as compare to non-integrated surface (Green). This is the validation and confirmation of our result for soft and hard substrate.

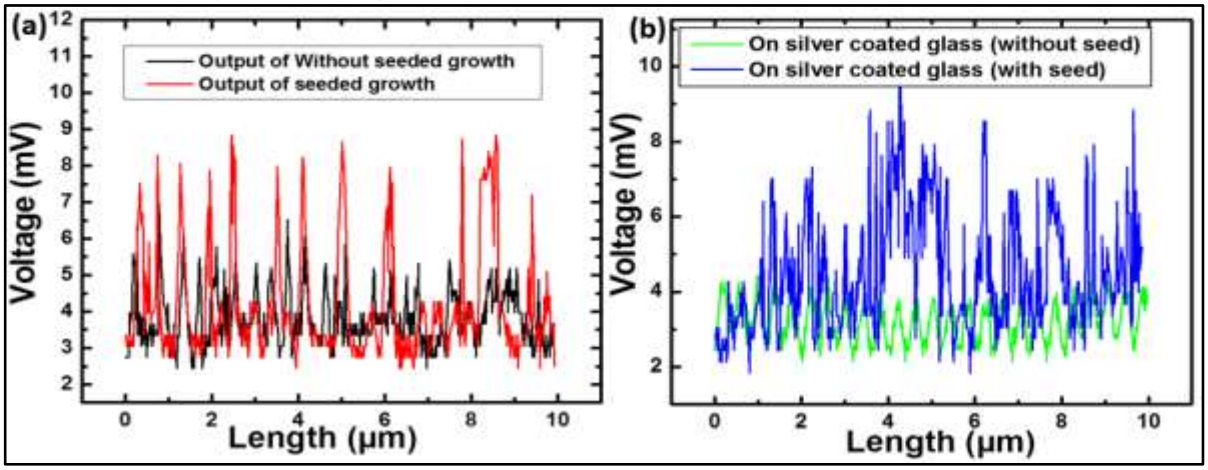

Fig. 7 *2D images of generating piezoelectric potential from ZnO nanorods grown on (a) Graphene coated plastic substrate, (b) Sliver coated glass substrate.*

Conclusion

This investigation reveals the fact that the surface integration can play a crucial role in the mechanical and piezoelectric performance of electronic devices. The growth density, high mechanical stability and large elastic recoveries are indication of differentiation in performance of integrated and non-integrated surfaces. Similarly the amount of measured piezoelectric potential also show the high outputs from integrated surface. It is also important to highlight that both soft and hard substrates showed almost similar kind of surface integration effect. This approach will be fruitful for research community as it reveals the importance of surface modification for fabrication of good result oriented devices.

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