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Characterization of ion irradiated silicon surfaces ablated by laser-induced breakdown spectroscopy

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Low energy metallic ions, generated by a Q-switched Nd:YAG laser (1064-nm wavelength, 10-mJ energy, 9-nm ∼ 12-ns-pulse width, 10^{11} W/cm^2 intensity) irradiated on a silicon substrate to modify various properties, such as electrical, morphological, and structural modifications. Thomson parabola technique is used to calculate the energy of these metallic ions whereas the electrical conductivity is calculated with the help of Four-point probe. Interestingly circular tracks forming chain like damage trails are produced via these energetic ions which are carefully examined by optical microscopy. It is observed that excitation, ionization, and cascade collisions are responsible for surface modifications of irradiated samples. Four-point probe analysis revealed that the electrical conductivity of substrate has reduced with increasing trend of atomic number of irradiated metallic ions (Al, Ti, Cu, and Au). The x-ray diffraction analysis elucidated the crystallographic changes leading to reduction of grain size of N-type silicon substrate, which is also associated with the metallic ions used. The decreasing trend of conductivity and grain size is due to thermal stresses, scattering effect, structural imperfections, and non-uniform conduction of energy absorbed by substrate atoms after the ion irradiation.

Keywords: ablation, Thomson parabola technique, four-point probe

PACS: 74.25.Kc, 61.80.Ba, 61.80.Lj, 61.82.–d **DOI:** 10.1088/1674-1056/27/8/087401

1. Introduction:

Nanofabrication of semiconductors through irradiation of laser plasma-generated ions has yielded a variety of systematic nanostructures. Stress generation, modification of cascade collisions, and formation of silicides are probable impurity defects in irradiated silicon.[1] Past few years, the pulsed laser irradiation of silicon and other metal surfaces have been a dynamic field of research in the field of materials science that have led a number of surprising results.[2] Laser irradiance has been used to understand the specific phenomena of different processes, including electron–hole plasma formation,[3,4] ablation,[5] and ultrafast melting.[6–8] Laser irradiation is also used as an alternative method for annealing ion-irradiated semiconductors.[9] Generally, the laser irradiation of materials generates many complex changes within the material including electrical, optical, morphological, structural, etc.[10–12] These kind of modifications in irradiated samples induced by laser irradiation strongly depend upon both, the laser parameters and properties of target material[13]

Silicon is a widely accessible semiconducting material because of its abundance on earth after oxygen. Metal-irradiated silicon has promising applications in formation of solar cells, biosensors, nano, micro and optoelectronics.[14] Electrical characteristics and mechanical adhesion of metal semiconductor have tremendous usage in device applications like packaging and normalization.[15] Nano fabrication of silicon has remarkable functionalities in the field of research and industries by exhibiting unique mechanical, optical, and electronic properties. For this purpose, several efficacious fabrication techniques have been used like electrochemical etching, oxide assisted growth, laser ablation, and chemical vapor deposition.[16] At the early stage, chemical etching techniques are used for nanofabrication of silicon whereas later on, physical techniques like laser ablation and metal ion irradiation techniques are also introduced. Radiation-induced silicon devices have a variety of application in the field of particle accelerator, nuclear plants, and in space as well.[11,17,18] Radiation-induced damage in silicon semiconductor material may reduce charge collection properties and thus showing interest in producing position-sensitive sensors. This approach may be utilized for the production of silicon pin diodes.[19]

In the current research project, four metals (Al, Cu, Au, and Ti) are irradiated by Q-switched table top Nd:YAG laser and the corresponding energetic ions are irradiated on the n-

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type silicon substrate. Various characterization techniques have been used to analyze the morphological, electrical, and structural modifications induced in the substrate as a consequence of low energy metallic ions irradiation.

2. Materials and methods

The experimental set up used in the present research work consists of an eight-port stainless steel vacuum chamber with Nd:YAG laser system as shown in Fig. 1.[20] The four metal targets (Al, Au, Cu, and Ti) have been irradiated separately by 300 laser shots through Nd:YAG laser system at $\sim 10^{-3}$ Torr (the unit 1 Torr $= 1.33322 \times 10^2$ Pa). The Nd:YAG laser is tightly focused (with germanium-coated IR Plano-convex lens of the focal length 17 cm) on these metal targets which initiate ablation. The laser-generated ablated plasma acts as ion source and the n-type silicon act as a substrate which is placed at 9-mm distance from the targets. Five samples of silicon with 0.25 mm $\times$ 8 mm $\times$ 8 mm dimensions are prepared by a diamond cutter. Then all samples are cleaned with de-ionized water and after drying, irradiated by the metallic ions. During the irradiation of the metal targets, the target is kept at an angle of 45° with respect to the normal of target surface in order to get maximum plume formation. The energy of these irradiated metallic ions is measured by the Thomson parabola technique.

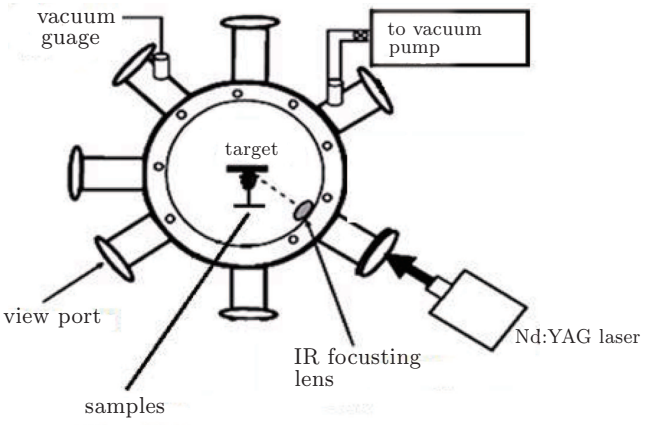


Fig. 1. Schematic diagram of stainless-steel vacuum chamber.

As the energy of the laser-generated metallic ions depends on various parameters such as atomic number, melting point, and thermal conductivity, etc. The low melting point plays an important role in ejection of material having more flux. Energies of the metallic ions have been presented in the floowing Table 1. The energy of aluminum metal ions is 178 keV which is higher in comparison with the other metallic ions which attribute to the fact that its atomic number is lesser as compared to other metals and lighter mass enables the Al ions to remove faster and accelerate away towards the substrate with greater velocity.

Table 1. Energy of metallic ions used in this research work.

Name of elements	Atomic number	Energy/keV
Al	13	178
Ti	22	157
Cu	29	114
Au	79	27

3. Results and discussions

3.1. Surface morphology

Surface morphology of pristine and laser-generated plasma ion-irradiated silicon substrate has been analyzed using optical microscope at resolution of 10$\times$ as shown in Fig. 2. It is obvious in Fig. 2(a) that the surface of un-irradiated Si is very smooth and clear. After the irradiation of metallic ions (Al, Ti, Cu, and Au) on Si substrate, it is observed in Figs. 2(b)-2(e) that circular tracks forming chain like damage trails appear at the surface of the substrates. It is also observed that the cores of these tracks are not of the same diameter. Some tracks are smaller and some are bigger in diameter. These tracks attributed the fact that the ions emitting from the plasma plume are of different energies depending upon their charge states. Once these energetic ions interact with the surface of the substrate, their energies will be transferred to the surface atoms hence leading them towards the excited states.[21] After excitations, these atoms then tend to vibrate with higher amplitude and are displaced from their initial lattice sites.[20] Laser-induced plasma ions keep on transferring their energy to the substrate atoms until they completely reach at rest position. In this way, an ion track of cone-like shape is formed. The vertex of the ion track is the point at which the ion meets the substrate atoms. Collisions generated by the interaction of ions with substrate atom produce cascades and sub-cascades of collisions. These collisions are also responsible for the structural disorder of material.[19,22] Thus, it may also happen that higher the energy of ions, more will be displacement of atoms hence producing ions track cores of larger diameter.[13–15] These ion tracks confirm the irradiation of ions within the substrate. Penetration depth of ions depends upon their energy.[23] A high energy ion penetrates more such that it causes excitation of a large number of atoms. This may lead to the structural modifications as observed in this experiment. It has been observed that incoming series of ions may get irradiated on the same tracks formed previously irradiated ions. Due to track overlapping, non-circular shapes are formed.

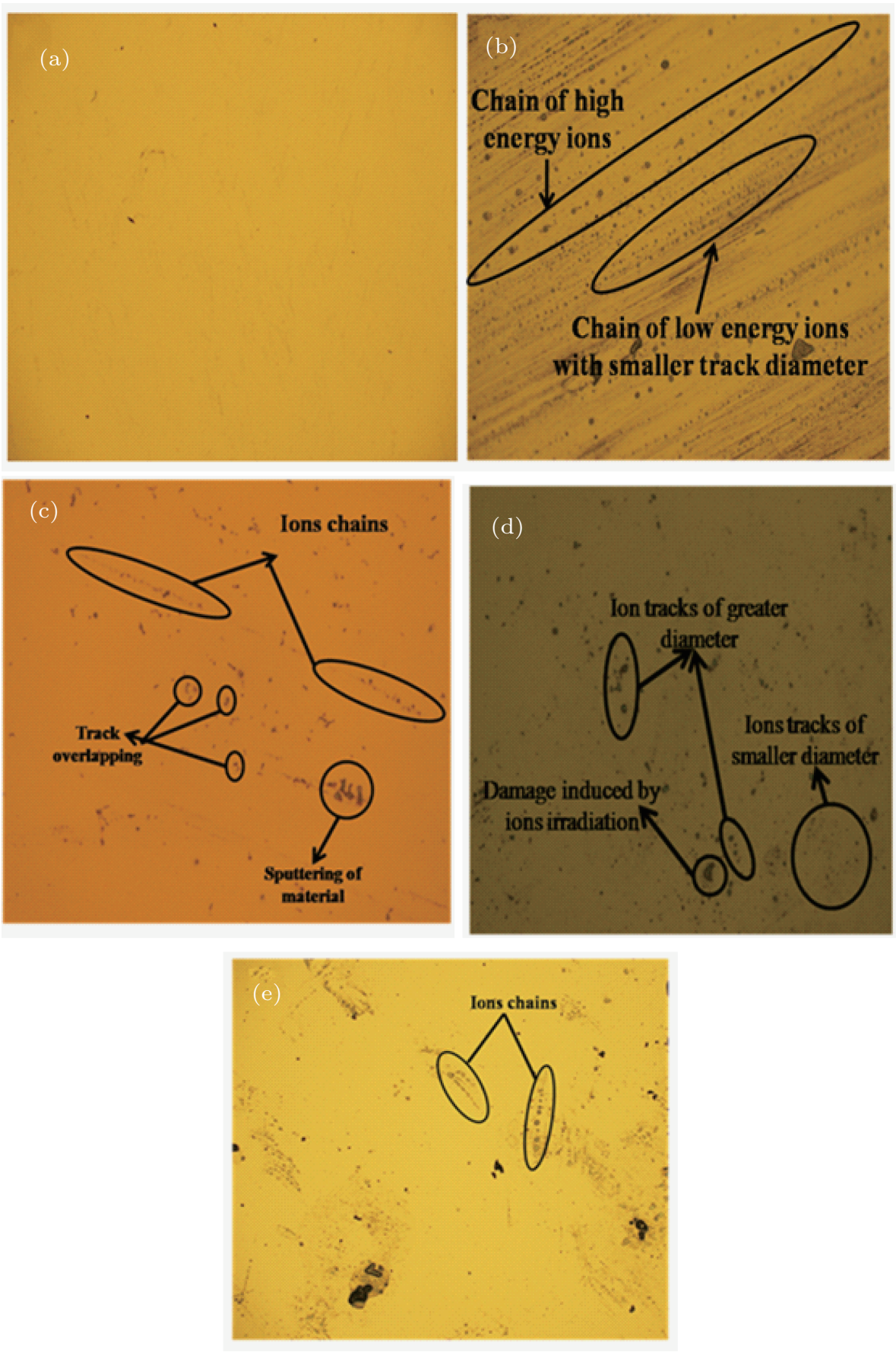


Fig. 2. (color online) Optical micrographs of (a) pristine N-type Si, (b) Al ions irradiated, (c) Ti ions irradiated, (d) Cu ions irradiated, and (e) Au ions irradiated n type Si.

3.2. Electrical properties

Electrical properties of pure- and ions-irradiated silicon has been depicted in Fig. 3. The irradiated ion makes collisions with the substrate atoms and transfers its energy to the substrate atoms setting them to be displaced from their original lattice points thus creating vacancies at interstitial sites and deep centers. Finally, after liberating all its energy, it comes to rest with substrate atom by making substitutional site. These interstitials draw some stresses on the neighboring atoms and cause the disturbance in their orientations in the crystal structure which further leads to the structural imperfections. Deep centers are also formed in substrate due to presence of more vacancies after irradiation and part of them (vacancies) can either connect with each other or can be captured by metallic atoms.[11] Thus, due to formation of these deep centers and structural imperfections in substrate material the forbidden gap of silicon crystal increases and conductivity decreases because the main carriers captured by radiation defects centers do not take part in conductivity.

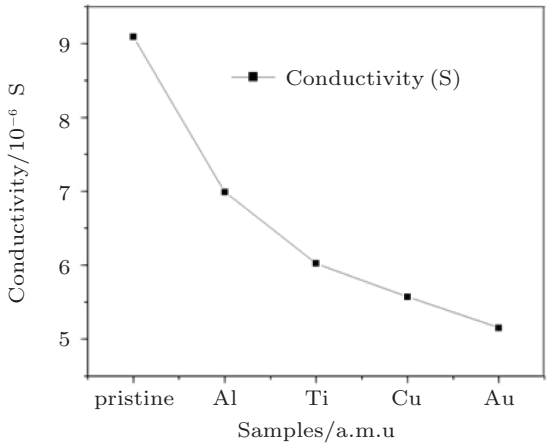


Fig. 3. Variation in electrical conductivity of metallic ion-irradiated silicon substrate.

Due to the interaction of irradiated ions with semiconducting material some electrically active defects are created which may result in variation of electrical parameters of semiconductor materials, e.g., enhancement of resistance because of reduced ionized donor concentration.[23] It is elucidated that radiation-induced damage either acting as trapping centers for majority carriers or they compensate with majority carriers thus decreasing the current flow and increasing the resistivity after irradiation. So the decreasing effect of conductivity of semiconductor material can be linked with decreasing of carrier mobility. This is also known as carrier removal phenomenon under which effective current carriers are trapped by radiation induced damage.[24] Carrier removal is a substantial characteristic of displacement damage. Low energy ions of keV range contribute to nuclear energy loss thus assisting displacement damage to feature the carrier removal phenomenon. Because of this radiation-induced defects depletion region get widens than the range of irradiated ions which may become the reason of decreased conductivity after irradiation. During ions irradiation, the number of structural defects increases which leads to decrease of grain size. Micro-strain increases with increasing of number of pulses. Since micro-strain is related to distortion of structure, the increase of micro-strain could be assigned to high concentration of irradiation-induced defects and dislocations.

3.3. Structural analysis

Irradiation of laser-generated metallic ions on silicon substrate produces some structural imperfection as well by producing stresses within the material. Such irradiation further leads to variation in grain size. This variation results in the defects formation in structure of the substrate. The x-ray diffraction (XRD) pattern of un-exposed silicon is shown in Fig. 4(a). The XRD pattern of un-exposed silicon sample has three peaks. The intensities of these peaks are at 28.44°, 47.31°, and 56.13°. The planes corresponding to these peaks are (111), (022), and (113) with the maximum value of intensity at peak of 2θ position 28.45°. The plane corresponding to this position is (111) which is well known in literature. The data obtained from the XRD pattern are further used to calculate the grain size of the material before and after the irradiation of metallic ions. The grain size of pristine sample turnout to be 43.15, 35.14, and 52.65 nm at (111), (022), and (113) corresponding planes respectively. It is observed that the pure silicon is a crystalline in nature exhibiting very sharp peaks at the 2θ positions. The modification in silicon structure produced after the irradiation of Al, Ti, Cu, and Au ions has been shown in Figs. 4(b)–4(e) respectively. In Fig. 4(b) the appearance of peaks at 2θ corresponding to 38.46° and 44.71° confirmed that the Al ions have been irradiated within the material. It causes the material to change its structural properties such as decrease in grain size. Now the grain size has reduced to 42.09, 33.89, and 51.07 nm at (111), (022), and (113) corresponding planes respectively. The θ position of bot exposed and unexposed samples is the same, however slight variation has been observed in peak intensities. The slightly decreased peak intensity of exposed sample is due to thermal stresses, scattering effects, and non-uniform conduction of energy absorbed by atoms.[19,21] For both exposed and unexposed samples d-spacing is the same which predicts that energy of exposed Al ions (178 keV) is not enough to change the spacing of planes. While the grain size is specifically decreases after irradiation of Al ions as a result of induced thermal stresses. This decrease causes the material to become more resistive in nature. Similar is the case with the irradiation of Ti ions

silicon substrate as represented in Fig. 4(c). In this case the peaks of XRD pattern appearing at the positions 38.418° and 55.459° represent the peaks of titanium metal ions within the Si substrate. The grain size of Ti-irradiated substrate is 43.00, 32.14, and 49.61 nm at (111), (022), and (113) planes respectively which also predicts the decreasing trend as compared to irradiated sample. The irradiation effects of copper ions on silicon substrate are clearly observed from the XRD pattern given in Fig. 4(d). The peaks appearing at positions at 32.179 and 35.390 gives the confirmation about the irradiation of copper ions within substrate. The calculated grain size in this case also depicts the decreasing behavior. The calculated grain size in this case is 43.00, 33.29, and 50.40 nm at (111), (022), and (113) planes respectively. Similarly, from Fig. 4(e) additional peaks of Au metals at the 2θ positions 38.26° and 44.47° appear within the Si substrate. These peaks are the evidence of the presence of Au ions within the Si substrate. The calculated grain size in this case also represents the decreasing behavior having the values of 39.09, 37.89, and 51.78 nm at (111), (022), and (113) planes respectively.

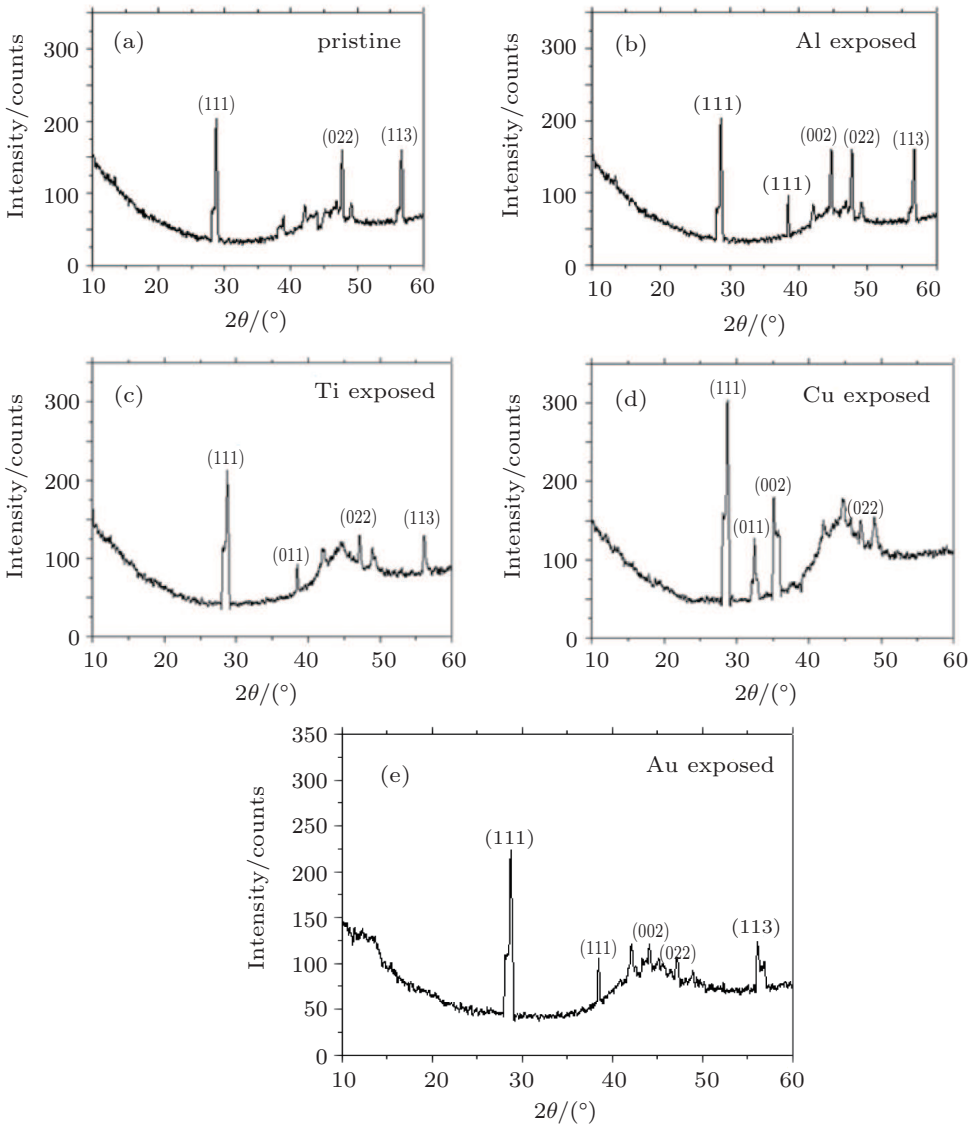


Fig. 4. (a) XRD pattern of n-type silicon before irradiation whereas panels (b), (c), (d), and (e) represent XRD patterns of substrate after irradiation of Al, Ti, Cu, and Au, respectively.

A comparative analysis between the irradiation effects of metallic ions on the silicon substrate show that after irradiation the grain size of substrate decreases specifying partial texturing of material. There is no significant peak shifting observed after irradiation except in case of copper. It is also observed that the intensity of the peaks decreases after irradiation. When the irradiated metallic ions excite the atoms of exposed part, they tend to dislocate from their initial positions. The dislocations of atoms tear the bigger grains of the exposed structure into the smaller grains which shows that the sample has an amorphous behavior after the laser irradiation.[16] The decrease in intensity and grain size are the evidence that the substrate has undergone through some structural imperfections. These imperfections alter the structural properties such

as a major effect is observed on the conductivity of the silicon substrate.

4. Conclusion

Metallic targets (Al, Ti, Cu, and Au) have been irradiated by Nd:YAG laser using 300 laser shots that results in production of metallic ions through plasma generation. Metallic ions irradiated on silicon substrates have been analyzed by optical microscope, four-point probe and x-ray diffractometer to elucidate surface morphological, electrical, and structural properties, respectively. It is observed that ions irradiation leads to the change in surface morphology by developing circular track cores and ions chains. The size of diameter of ion tracks strongly depends upon energy of incident ion. It is concluded that Al ions are more energetic in comparison with other metallic ions. The irradiation of metallic ions on substrate causes the decrease in electrical conductivity with respect to their pristine value. After irradiation grain size reduces due to thermal stresses induced by structural imperfection as analyzed by XRD.

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