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Enhanced electrochemical etching of ion irradiated silicon by localized amorphization

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A tailored distribution of ion induced defects in p-type silicon allows subsequent electrochemical anodization to be modified in various ways. Here we describe how a low level of lattice amorphization induced by ion irradiation influences anodization. First, it superposes a chemical etching effect, which is observable at high fluences as a reduced height of a micromachined component. Second, at lower fluences, it greatly enhances electrochemical anodization by allowing a hole diffusion current to flow to the exposed surface. We present an anodization model, which explains all observed effects produced by light ions such as helium and heavy ions such as cesium over a wide range of fluences and irradiation geometries. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4876917]

Ion irradiation of semiconductors causes damage in which lattice atoms are displaced from their initial locations.[1–4] We previously showed how low fluence irradiation of p-type silicon with highly focused light ions, such as 30 keV helium, induces a "current funneling" effect[5,6] during subsequent electrochemical anodization.[7,8] For such low energy ions, the peak of defect density occurs very close to the irradiated surface.[9] A portion of these defects act as hole traps, resulting in the effective doping concentration being a minimum very close to the surface. During electrochemical anodization the diffusion component of the hole current is focused or "funneled" towards the surface along the gradient of reduced dopant density, resulting in a greatly enhanced local anodization current density,[5] formation of highly porous silicon, and enhanced photoluminescence.[6]

Simulations of the hole current flow during anodization predicted that high fluence irradiation (i.e., the fluence is high enough to stop anodization, producing surface or 3D silicon machined patterns after anodization) fully depletes the hole density within the irradiated volume;[5] no hole current flows through such a high resistivity volume during anodization, so it remains as crystalline silicon. For high ion energies of hundreds of keV, the maximum defect density is a few micrometers beneath the wafer surface; at shallower depths there lies a zone where the defect density is fairly uniform. Exclusion of hole current flow from the end-of-range peak containing a high defect density was demonstrated,[10,11] and the resultant buried silicon wires used to fabricate a variety of 3D micro- and nano-scale structures with applications in a variety of fields,[12–15] such as components for silicon photonics and for MEMS (microelectromechanical systems) and photonic lattices. However, for low ion energies, such as 30 keV helium, experimental results do not agree with simulations; instead, following anodization, a dip is observed at the center of lines irradiated at high fluences. Clearly, an additional factor contributes to anodization at high fluences, which is not accounted for in simulations, which assume that the irradiated volume remains fully crystalline. We show here that chemical etching of the localized, amorphized region induced by ion irradiation results in enhanced electrochemical anodization by enabling a hole current to flow, which would otherwise be prevented from passing through a depleted region. We combine effects due to chemical etching and electrochemical anodization of p-type silicon in a hydrofluoric acid (HF) electrolyte into a model, which describes all phenomena observed for 30 keV helium ion irradiation over a wide range of fluences and irradiation geometries. We demonstrate that this model can be used to predict and explain all anodization effects produced by low energy, heavy ion irradiation such as 15 keV cesium ions, which have a range of ∼30 nm.

Fig. 1(a) shows the defect density produced by 30 keV helium ions in silicon, calculated using SRIM (Stopping and Range of Ions in Matter).[9] The ion range is about 450 nm, and for broad beam irradiation (i.e., the irradiated surface area is larger than the beam spreading at the end-of-range), the defect density profile peaks at ∼250 nm beneath the surface. The defect density, and hence the majority carrier depletion, does not increase towards the surface, so there is no mechanism to induce a significant diffusion current towards it. For such broad beam irradiation, there is no lateral gradient of defect density, except at the edges of the irradiated region, so only here one observes a significant diffusion current flow, as observed in Ref. 6. In comparison, Figs. 1(b) and 1(c) show the defect distribution produced by the same ions focused to a small probe size of <1 nm in a helium ion microscope.[16] Under these conditions, there now exists a strong gradient of increasing defect density towards the surface so one expects a strong diffusion current funneled to the surface during electrochemical anodization, producing a dip owing to a faster etching rate. Comparison of the anodization behaviour of silicon irradiated in focused and broad beam geometries thus provides an insight into the significance of diffusion current funneling, since it is expected in the former irradiation geometry but absent in the latter. The same study