Etching of Germanium by Chlorine Gas using a Focused Electron Beam

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Resistless etching in the nanometer scale has a wide range of applications including chip or mask repair. Material removal by focused ion beam technique is well established but has the disadvantage of significant gallium implantation into the substrate and amorphization of the substrate. In order to overcome this disadvantage it is desirable to use electrons because an etching process involving only electrons will remove material solely chemically in the absence of physical sputtering. This implies that this method requires a specific etching agent for each substance that shall be removed. Several successful etching processes with a focused electron beam induced reaction on different substrates, for instance silicon or silicon oxide have been reported several times in the literature [1,2,3]. However, no focused electron beam induced etching process for germanium, which is considered a potential future replacement for silicon in semiconductor industry (in conjunction with high-*k* dielectrics), has been reported until now.
Using pure chlorine (Cl_2) as etchant it is possible to convert solid germanium into volatile germanium tetrachloride (vapor pressure: ~80 mbar at 20 °C):

$$Ge + 2Cl_2 \rightarrow GeCl_4$$

We present a detailed experimental analysis of an electron beam induced etching process of germanium using chlorine gas as precursor. The process was carried out using a conventional gas injection system (GIS) setup in a scanning electron microscope (SEM). The Cl_2 supply is regulated by a mass flow controller. The entire GIS is adapted to work with highly corrosive and toxic substances.

We demonstrate the etching of a crystalline germanium substrate using pure chlorine gas which is introduced into the SEM chamber by means of a conventional GIS. The efficiency of the etching process was observed to be up to 15 nm per minute for an area of 1.5x1.5 µm². The influence of various etching parameters such as electron beam current, acceleration voltage, dwell time, and chlorine gas flow on the etching efficiency as well as the shape of the etch pits have been studied systematically by AFM analysis.
It is also demonstrated that etching amorphous germanium films can be facilitated significantly faster (~8 times) than etching of crystalline germanium.

For the first time, a well-controllable, direct-write, resistless and non-destructive etching process for germanium using a focused electron beam with nanometer resolution could be developed. It allows for precise and efficient removal of germanium from a surface without showing any spontaneous etching effects.

References

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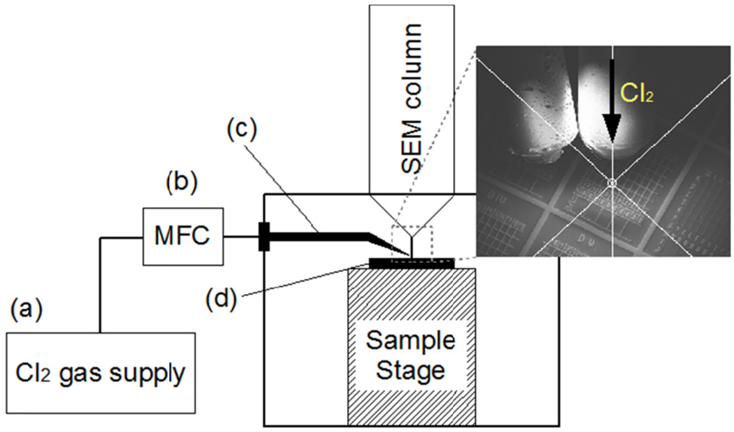
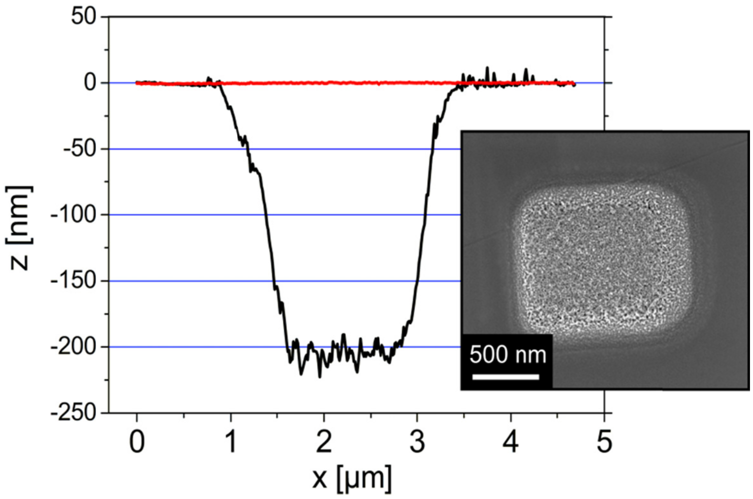


Fig. 1: Schematic view of the experimental setup employed for electron beam induced etching with chlorine. a) contains the chlorine gas cylinder with valves and nitrogen purging capability, (b) depicts the mass flow controller which regulates the gas flow into the SEM chamber, (c) illustrates the GIS positioning system with two separate nozzles and (d) represents the sample.

Fig. 2: Etched crystalline germanium surface after **20 minutes** of focused electron beam induced etching treatment. The etch dimensions amounted to 1.5 × 1.5 µm². Etching was performed using 5 keV electrons at a beam current of 5 nA. The observed etch rate in this case calculates to 10 nm per minute.



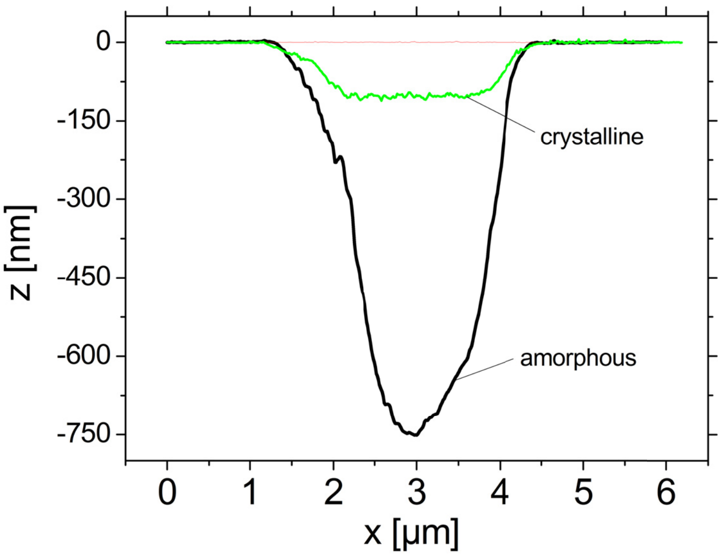


Fig. 3: Cross-section deduced from AFM analysis of an amorphous germanium film (created by RF-plasma sputtering) treated by focused electron beam induced etching (thick, black, solid line). Processing took place for **10 minutes** using 5 keV electrons at a beam current of 5 nA. For comparison purposes, the same etching parameters have been applied to a crystalline germanium sample (green, solid line). The data show that etching of amorphous germanium can be facilitated up to 8 times faster than etching of crystalline germanium.