Formation of Pyramidal-shaped Etch Pits on Germanium Surfaces Using Catalytic Reactions with Metallic Nanoparticles in Water

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1. Introduction

Recently germanium (Ge) has attracted attentions not only in the field of microelectronics, but also in that of micro-optics, because of its unique optical properties. They are the high dielectric constant (ϵ (Ge)=16.2) and the small bandgap (0.66 eV), which motivate researchers to fabricate optical devices such as a photonic crystal and a solar cell. A pore formation on a Ge substrate is a key process to develop these Ge-based optical devices. Either dry or anodic (electrochemical) etching may be used to fabricate pores, which requires complicated processes or special equipments, however. In contract, a metal-assisted etching is attractive because of its simplicity and low cost. Many works have been made on this issue on a silicon (Si) substrate with noble metals in aqueous solutions including mainly HF and H₂O₂ [1-3]. The mechanism is the selective oxidation of the interface between noble metals and a Si substrate, and subsequent etching of the oxide in an HF solution. The Ge oxide (GeO_2) is soluble in water, which is a unique chemical property for Ge. This is sometimes a problem in forming gate stacks in MIS (metal-insulatorsemiconductor) structures, but gives us another opportunity to form nanostructures on a Ge surface. In this study, we present an environmentally friendly formation of pits on Ge with metallic nanoparticles in water. We also discuss a possible mechanism by electronic energy relationships.

2. Experimental

A Ge wafer used in the present study was p-type Ge(100) with 10-12 Ω cm. It was first treated with a UV/ozone generator for 15 min in order to remove organic contaminants, and was immersed into a diluted HF solution (0.5%) for 1 min. We used two kinds of metallic nanoparticles (Pt and Ag). In the case of Pt, the Ge sample was immersed in a solution containing synthesized nanoparticles with the size of approximately 7 nm, and dried by N₂. On the other hand, Ag nanoparticles with the size of approximately 20 nm were deposited on the Ge surface by dipping it into a mixed solution of HCl (10⁻³ M, 100 ml) with AgClO₄ (10⁻⁴ M, 100 ml) for 5 min [4]. After dipping, it was dried by N2. The Ge sample with the metallic particles was immersed into semiconductor-grade water for 24 hours for a pore formation. A surface structure after the immersion was observed by a scanning electron

microscope (SEM).

3. Results and Discussion

Figure 1 shows typical SEM images of the Ge surface with either Pt or Ag nanoparticles. Figure 1(a) and 1(b) shows the Ge surface with Pt nanoparticles before and after the immersion into water, respectively. The scanned areas are different in the two images. It is clear that the bright protrusions in Fig. 1(a) corresponding to Pt particles disappear and many pits are formed instead after the water immersion as shown in Fig. 1(b). It should be noted that the shapes of the pits are neither circular nor irregular, but square. This trend is observed in the Ag particles as well, as shown in Figs. 1(c) and 1(d). A magnified SEM image in the inset of Fig. 1(d) indicates that the pit has a pyramidal shape with a metallic particle remaining at the bottom.

Figure 2(a) shows a cross-sectional SEM image of a pit on the water-immersed Ge surface with the Ag particles. The angle of the slope to the (100) surface is estimated to be 54°. Figure 2(b) is a schematic representation of the cross-sectional cut of the atomic distribution in the (110) plane. Another experiment revealed that the shape of etch pit on a Ge(111) surface was not pyramidal as we find in Figs. 1 and 2, but triangular. These results demonstrate that both Pt and Ag nanoparticles on Ge surfaces promote anisotropic etching to expose (111) facets in water.

The next question is the mechanism to induce the selective etching around metallic particles. We believe a key reaction is related to a familiar anodic oxidation, as shown below.

$$Ge + 2H_2O + 4h^+ \rightarrow GeO_2 + 4H^+$$
 (1)

Thus we should pay attention to the behavior of holes at the two different interfaces (metallic particles/Ge surface, and water/Ge surface) in the system. H^+ ions in eq. (1) are expected to be released as H_2 gas in water.

Figure 3 shows the energy band diagrams of the systems in which the electron affinity (χ) and the bandgap of Ge are 4.05 eV and 0.66 eV, respectively. It is widely accepted that the redox coupling at zero pH is defined as the normal hydrogen electrode (NHE) with a potential of 4.44 eV with respect to vacuum [5]. This enables us to translate the measured redox potential of water

(approximately 0.6 eV [6] vs. NHE) into a potential with respect to vacuum (5.04 eV). Figures 3(a) and 3(b) represent the electronic energy relationships at the water/Ge and the Pt/Ge interface, respectively. Because the work function of Pt (5.65 eV [7]) is larger than the water potential, more holes are accumulated at the Pt/Ge interface than the other. This accelerates the Ge oxidation in eq. (1) around Pt particles, which results in the pits in Fig. 1(b) after the oxide is dissolved in water. Figures 3(c)-3(e) show the case of Ag nanoparticles. Figure 3(c) (water/Ge interface) is the same as that in Fig. 3(a). Figure 3(d) is the energy relation at the Ag/Ge interface with the nominal work function of an Ag bulk (4.26 eV) taken from the literature [7]. Figures 3(c) and 3(d) indicate that the Ag particles attract less holes in Ge than surrounding water, which contradicts to the SEM result in Fig. 1(d). In order to explain this discrepancy, we must draw attention to the variation of work functions depending on the size of Ag particles. It has been reported that the work function of Ag particles increases from 5.29 eV to 5.53 eV as the particle size decreases from 35 nm to 4 nm due to a thin oxide layer on the particles [8]. These values are approximately 0.8 eV higher than for an Ag bulk. If we assume the work function of the Ag particles in our experiment to be 5.40 eV, the band diagram at the Ag/Ge interface changes from Fig. 3(d) to Fig. 3(e), which gives a reasonable explanation for the pits in Fig. 1(d).

We expect that the oxidation rate by the catalytic effect with metallic particles changes depending on surface orientations. In other words, the rate of the (111) facet is slower than that of the (100) facet, which is the reason for the "pyramidal" shaped etch pits as shown in Fig. 2(a).

4. Conclusion

We demonstrated a method to form pyramidal shaped etch pits on a Ge(100) surface in water. This method is composed of two processes. One is the catalytic oxidation of the Ge surface by metallic nanoparticles, in which the catalytic property can change if the particles are partially oxidized. The other is the dissolution of GeO₂ in water. This presents a possibility to develop the novel process to form pores for future micro-optics, which is totally eco-friendly without any waste fluid including chemicals.

Finally it should be noted that the result is also very important in microelectronics, especially in understanding the behavior of metallic residuals on Ge surfaces during wet cleaning processes.

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Fig. 1. SEM images of Ge(100) surface with metallic particles. (a) Pt particles with diameter of around 7 nm. (b) After immersion of the surface in (a) into water for 24 hours. (c) Ag particles with diameter of around 20 nm. (d) After immersion of the surface in (c) into water for 24 hours.



Fig. 2. (a) Cross-sectional image of pyramidal-shaped etch pit after catalytic reaction in water with Ag particle. (b) Schematic drawing of the cross-sectional cut of atomic distributions in the (110) plane. Open and closed circles represent bulk and surface Ge atoms, respectively.



Fig. 3. Schematic view of band diagrams. (a) Water/Ge interface, (b) Pt/Ge interface, (c) Water/Ge interface (same as (a)), (d) Ag/Ge interface. A bulk work function is assumed for Ag. (e) Ag/Ge interface. The work function for a nanoparticle is assumed.