Conclusions

A highly successful procedure has been developed which allows deposition of thin-film ceramics on highly porous substrates. The methodology is inexpensive and scalable. Thin-film SOFCs fabricated using these techniques demonstrate performances of close to 2 W/cm² at 800°C. Current interrupt techniques indicate the majority of the voltage loss at high current density is due to ohmic losses, most likely associated with cathode/electrolyte contact resistance (0.1 Ω cm²). The exceptional performance of the thin-film SOFCs implies that reduced temperature operation is possible while maintaining high power density.

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Highly Selective Chemical Etching of Si vs. Si<sub>1-x</sub>Ge<sub>x</sub>

Using NH₄OH Solution

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ABSTRACT

Highly selective chemical etching of Si vs. epitaxial Si<sub>1-x</sub>Ge<sub>x</sub> in NH₄OH solution has been investigated. It was found the selectivity was better than 80:1 even for a SiₓGe<sub>1-x</sub> in 10 weight percent (w/o) NH₄OH at 75°C. As the fraction x of Ge was increased, higher selectivity was obtained due to the decrease of the etch rate of the Si<sub>1-x</sub>Ge<sub>x</sub> The achievement of the excellent selectivity in a Si/Si<sub>1-x</sub>Ge<sub>x</sub> heterostructure was clearly demonstrated by scanning electron microscopy. Surfaces of etched Si<sub>1-x</sub>Ge<sub>x</sub> samples were analyzed using x-ray photoelectron spectroscopy. The high etch selectivity obtained in NH₄OH is essentially due to the passivation/film effect at the Si<sub>1-x</sub>Ge<sub>x</sub> surface.

Introduction

Selective chemical etching of Si or Si<sub>1-x</sub>Ge<sub>x</sub> has become a key technique in the fabrication of Si<sub>1-x</sub>Ge<sub>x</sub>/Si heterojunction device. In the fabrication process of the heterojunction device employing thin Si or Si<sub>1-x</sub>Ge<sub>x</sub> layers, for example, it is often necessary to contact to buried Si or Si<sub>1-x</sub>Ge<sub>x</sub> layers. To make contact to buried Si<sub>1-x</sub>Ge<sub>x</sub> layers one needs to etch Si and vice versa. Thin film bond and etchback silicon on insulator (BESOI) of good quality was fabricated using a strained Si<x>Ge<sub>x</sub> as an etch-stop layer. An important process of the fabrication was to selectively etch Si over the Si<x>Ge<sub>x</sub>. Recently, we proposed and successfully fabricated Si quantum wires based on selectively removing Si<sub>1-x</sub>Ge<sub>x</sub> from a Si/Si<sub>1-x</sub>Ge<sub>x</sub> trench array.

During the last several years, therefore, the characteristics of several chemical wet etchants for selectively etching Si<sub>1-x</sub>Ge<sub>x</sub> and/or Si on Si<sub>1-x</sub>Ge<sub>x</sub>/Si heterostructures have been investigated. Among them, two aqueous etchants to selectively etch Si over Si<sub>1-x</sub>Ge<sub>x</sub> were reported. One is the etchant composed of KOH:K₂CO₃:propanol:H₂O. Another is the mixture of ethyleneammoniium, pyrocatechol, and water (EPW), which was reported to etch Si over Si<sub>1-x</sub>Ge<sub>x</sub> (x > 0.2) with a high selectivity. For a practical application, however, a selective chemical etching should be compatible with silicon integrated circuit (IC) processes. As a result, IC-compatible, nontoxic, anisotropic, simple, and highly selective etchants become important for processing high performance devices. Solutions based on ammonium hydroxide-water mixtures have been widely used in Si IC processes. Koyama et al. investigated the etch characteristics of Si<sub>1-x</sub>Ge<sub>x</sub> alloy in an ammoniacal wet cleaning solution NH₄OH:H₂O. It was observed that the etch rate of Si<sub>1-x</sub>Ge<sub>x</sub> was in the order of...
manometers per minute and faster than that of Si, the result was suggested mainly because of the difference in microscopic reactions of Si and Ge with NH₃OH and H₂O. We first report here on highly selective chemical etching of Si with respect to epitaxial Si, Ge, alloy in NH₃OH solution. The selectivity was better than 60:1 for various Si, Ge alloys with different fractions x of Ge (0, 0.2, 0.3). Actually, the Si, Ge alloy acts as an etch-stop layer.

Scanning electron microscopy (SEM) was used to observe the cross section of a selectively etched Si/Si, Ge/Si heterostructure. The change in the surface chemical states of etched Si, Ge was analyzed using x-ray photoelectron spectroscopy (XPS). The results observed suggest that a very thin porous oxide layer as passivation film forms on the Si, Ge surface in NH₃OH solution, effectively depressing the etch rate of Si, Ge, and consequently resulting in very high etch selectivity.

**Experimental**

Undoped Si, Ge (x = 0.1, 0.2, 0.3) epitaxial films were grown on p-type (100) Si wafers by very low pressure chemical vapor deposition (VLCVD). These as well as (100) Si wafers were used as samples. Beside these, a Si/SiGe/Si sandwich structure was grown and used for observation by SEM. The thickness of epitaxial Si, Ge, and Si were about 150 nm. The details of the growth technique have been reported elsewhere. ¹⁴ SiGe patterns were formed by conventional SiGe chemical vapor deposition and photolithography technique on the top of the samples. Chemical etching was performed using 10 w/o NH₃OH solution at 57°C in a temperature-controlled system with a reflux condenser. SiGe patterns were first dipped in diluted HF for a few seconds to strip the native oxide, rinsed thoroughly in deionized water, and then immediately placed in the etch bath and etched with different etch times. After etching both SiGe patterns and the oxide formed on the surface of the etched parts in the etching procedure were removed completely by diluted HF. Etch depths of samples were measured using a Tencor Instrument Alpha step profilometer.

To analyze the cross section of Si/SiGe/Si etched under this condition, we carried out the experiment with a Si/SiGe/Si sandwich structure sample in the same etch condition. Here, lithography and reactive ion etching were carried out to generate line-and-space Si/SiGe/Si trench array along with (011) direction. SiGe pattern acted as a mask, protected the (100) facet of the sample from etching, while the two sides of the array consisting of (110) facets were exposed to etch.

Moreover, XPS study of etched Si, Ge, surfaces was conducted. Three as-grown SiGe, samples were HF cleaned first, washed in deionized water, and then two of those samples were put into the NH₃OH etchant for 0.5 and 1 h, and then were placed into a high vacuum chamber to perform measurement.

**Results and Discussion**

Figure 1a shows the results of the etch depth vs. the etch time in 10 w/o NH₃OH solution at 75°C. It can be seen that the relation between the etch depth and the etch time is almost linear for each sample with different Ge fractions (x = 0.3). Consequently, the etch rate is derived from the slope of the plot. It gives the etch rates of about 84 Å/min for Si, 7.4 Å/min for SiGe₉₀, 4 Å/min for SiGe₇₀, and 2.4 Å/min for SiGe₅₀ alloy, respectively, in 10 w/o NH₃OH at 75°C. The selectivity, defined as the etch rate ratio of the (100) Si to SiGe layer, as a function of Ge fraction x, is shown in Fig. 1b. Correspondingly, the selectivity is 86:1 for x = 0.1, 160:1 for 0.24, and 267:1 for 0.3, respectively.

Figure 2 shows a cross-sectional SEM image of an SiO₂/Si/SiGe/Si trench array after etching. The top layer is the SiO₂ mask. It can be clearly seen that the epitaxial Si layer was partly etched, its width reduced from 7500 to about 2000 Å. The etching of the Si substrate stopped at two (111) facets, forming a triangle trench. As expected, the Si, Ge layer was almost untouched in this etch process. It is known that defects usually affect the characteristic of a wet chemical etch. There are many defects in the epitaxial Si compared with the substrate Si. The observation shows similarity in etch characteristics for both epitaxial and substrate Si which demonstrates clearly that SiGe alloy is an excellent etch-stop layer in NH₃OH solution.

Si 2p photoemission spectra of the SiGe₀ samples are shown in Fig. 3. The photoemission peak at a binding energy about 99 eV is due to elemental Si, another peak near 110 eV is SiO₂. The corresponding Ge 2p photoemission spectra are shown in Fig. 4. The peaks at about 1218 and 1222 eV are assigned to elemental Ge and GeO₂, respectively. The intensities of both SiO₂ and GeO₂ peaks increase with increasing etch time. Moreover, the SiO₂, Ge peaks increase more obviously than the GeO₂. At the same time, the intensities of elemental Si and Ge peaks decrease regularly.

The above observations indicate that Si and Ge in samples were oxidized to form SiO₂ and GeO₂ in the etching process, and the oxides stuck on the surface of the SiGe, sample. Furthermore,
that the binding energy of SiO increases gradually to high energy demonstrates that the oxygen fraction x increases slightly with etch time and the oxide becomes the prevalent constituent. Being different from the thermal oxidation, the film composed of SiC and GeO₂ formed in water was a layer of porous oxide. Although porous, the oxide still acts as an effective passivating film on the surface of the Si₆₋Ge₄ film. In the etching process, hydroxide ions OH⁻ in the etchant must diffuse through the porous oxide layer and attack the sample. The oxide effectively reduces the concentration of the OH⁻ at the sample surface. This, in turn, decreases the etching rate of the Si₆₋Ge₄ drastically. For comparison, we investigated the etch of Si₆₋Ge₄ in aqueous KOH solution; it was much higher than that of SiC. One reason may be the higher concentration of SiO₃⁻ in SiC compared with that in SiC, which increases the oxide formation rate limiting. It is suggested that the mechanism of the etch stop of Si₆₋Ge₄ in Si₆₋Ge₄ is a passivation film effect.

With the observations above, the basis by which the oxidation in the film can selectively etched from Si₆₋Ge₄ layers is through the difference in the oxidation between the SiC and the Si₆₋Ge₄ layers in Si₆₋Ge₄. Compared with a surface consisting of only SiC film, the presence of Ge in the film results in a substantial number of weak Si-C bonds and Ge-containing bonds. This, in turn, decreases the etching rate and increases the etch stop. The etching of Si₆₋Ge₄ samples tends to form Si₆₋Ge₄ and GeO₂ film on the surface. Moreover, the defects in Si₆₋Ge₄ samples promote the oxidation process of SiC and GeO₂ to form Si₆₋Ge₄ and GeO₂ film.

This is supported by previous observations of enhanced oxidation at the surfaces of heavily doped silicon in KOH solution.

Moreover, Ge has been reported to act as a catalytic agent, which promotes the decomposition of SiO₂ to form more SiO₂. The more Ge fractions in Si₆₋Ge₄, the quicker the growth rate of Si₆₋Ge₄. Consequently, the etch rate of Si₆₋Ge₄ decreases with increasing Ge fraction.

**Conclusion**

We have reported on highly selective chemical etching of Si vs. epitaxial Si₆₋Ge₄ in NH₄OH solution. The selectivity for etching Si vs. the Si₆₋Ge₄ was better than 50:1, and higher selectivity was obtained as the Ge fraction x increased. The results presented here show that the NH₄OH solution is an excellent selective etchant for selectively etching Si vs. Si₆₋Ge₄. Consequently, the Si₆₋Ge₄ acts as an etch-stop layer. The SEM observation of Si₆₋Ge₄/Si heterostructure demonstrated that the Si₆₋Ge₄ alloy is an effective etch-stop layer. Moreover, the change in the surface chemical state of etched Si₆₋Ge₄ surfaces measured by XPS showed that a passive layer composed mainly of SiO₂ and GeO₂ formed at the surface in the etching process. The etch stop of the Si₆₋Ge₄ layer may be because the presence of Ge enhances the oxidation at the Si₆₋Ge₄ surface, and consequently the SiO₂ protects the Si₆₋Ge₄ from further etching in NH₄OH solution.

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