

Reaction of cyanide ions with copper on Si surfaces and its use for Si cleaning

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Abstract

A Si cleaning method has been developed by use of potassium cyanide (KCN) dissolved in methanol. When silicon dioxide (SiO₂)/Si(100) specimens with 10¹⁴ atom/cm² order copper (Cu) contaminants are immersed in 0.1 M KCN solutions of methanol at 25 °C, the Cu concentration is reduced to below the detection limit of total X-ray fluorescence spectrometer of ~3 × 10⁹ atoms/cm². X-ray photoelectron spectra show that the thickness of the SiO₂ layers is unchanged after cleaning with the KCN solutions. 10¹⁴ cm⁻² order Cu contaminants on the Si surface can also be removed below ~3 × 10⁹ atoms/cm², without causing contamination by potassium ions. UV spectra show that Cu-cyano complex ions are formed in the KCN solutions after the cleaning. The main Cu species in the KCN solutions is Cu(CN)₄³⁻ ions with the concentration of [Cu(CN)₄³⁻]:[Cu⁺] = 1:1.6 × 10²³. Even when the KCN solutions are contaminated with 64 ppm Cu²⁺ ions in the solutions, which form Cu(CN)₄³⁻ ions, the cleaning ability does not decrease, showing that Cu(CN)₄³⁻ ions are not re-adsorbed. The KCN solutions can also passivate defect states such as Si/SiO₂ interface states, leading to the improvement of characteristics of Si devices.

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1. Introduction

Copper (Cu) interconnects in large scale integration (LSI) have attained much interest because of the low resistivity, avoidance of electromigration due to higher melting temperature than that of conventional aluminum alloy, and the manufacturing cost reduction [1,2]. Since a minute concentration of Cu seriously degrades the device characteristics, i.e., decreasing the minority carrier diffusion length [3] and the minority carrier life time [4,5], increasing the interface state density [6] and surface roughness [7,8],

shifting the threshold voltage [9], etc. Although low concentration Cu contaminants do not strongly affect the leakage current density of thick (e.g., 5 nm) SiO₂ layers, they drastically increase that of ultrathin (i.e., less than 3 nm) SiO₂ layers [10], which are very important for currently produced LSI. Cu contaminants on the Si surfaces diffuse through the Si wafers even at room temperature [11].

Cleaning of Si devices during the LSI manufacturing processes is usually performed by use of the RCA method developed by Kern and Puotinen in 1970 [12]. The RCA cleaning method consists of several steps which include cleaning with ammonia peroxide, HCl peroxide, and diluted hydrofluoric acid (DHF). It is reported that metal contaminants such as Cu and Fe are removed by the combination of HCl peroxide, aqua regia, and sulfuric peroxide,

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but cannot be removed by the single cleaning process [10]. These cleaning methods require high temperatures at 50–80 °C, and moreover the cleaning accompanies etching of Si in nm order, which makes LSI fabrication processes very complicated. Recently, inclusion of chelating agents such as ethylene-diamine-tetraacetic acid (EDTA) in the cleaning solutions is found to decrease the metal concentration adsorbed on the surfaces [13,14].

In the present study, we have developed a defect passivation etch-less (DPEL) cleaning method by use of KCN solutions of methanol. The treatment with the KCN aqueous solutions has already been found to eliminate Si/SiO₂ interface states [15–17] and defect states in polycrystalline [18] and amorphous Si [19], resulting in the improvement of electrical characteristics of metal–oxide–semiconductor (MOS) diodes. We have recently found that KCN solutions of methanol have an ability of removing Cu and Ni contaminants from Si surfaces [20].

2. Experiments

Boron doped p-type Si(100) wafers with a $\sim 10 \Omega \text{ cm}$ resistivity were cleaned by use of the RCA method, followed by etching with 5 vol% hydrofluoric acid (HF) solutions. Then, 6.1 nm-thick SiO₂ layers were formed at 850 °C by wet-oxidation. The SiO₂/Si and Si(100) specimens were immersed in 0.1 M copper dichloride (CuCl₂) aqueous solutions at 25 °C for 30 min, and rinsed with methanol and ultra-pure water at 25 °C. For the removal of Cu contaminants, the specimens were immersed in 0.1 M (i.e., 0.65%) KCN solutions of methanol at 25 °C for 30 min, followed by rinse with ultra-pure water at 100 °C for 30 s. In another case, Cu-contaminated specimens were immersed in 0.1 M KCN solutions of methanol containing 1 mM (i.e., 64 ppm) CuCl₂. Cleaning of the Cu-contaminated Si wafers was also performed using 0.5% HF solutions. After all the chemical treatments, the specimens were dried with a fast stream of pure N₂ gas.

The surface Cu concentrations were determined using a total reflection X-ray fluorescence (TXRF) spectrometer (Technos TREX 610 spectrometer). The thickness of the SiO₂ layers was estimated from X-ray photoelectron spectroscopy (XPS) measurements by use of a VG Scientific Escalab 220i-XL spectrometer with a monochromatic AlK α radiation source. UV spectra were recorded with a JASCO V-570 spectrometer. Conductance–voltage (G – V) characteristics were measured using an HP 4192A LF impedance analyzer. Current–voltage characteristics for pn-junction single crystalline Si solar cells were measured under AM 1.5 100 mW/cm².

3. Results

Fig. 1 shows the TXRF spectra for the SiO₂/Si(100) specimens contaminated with Cu before (spectrum a) and after (spectrum b) the cleaning with the KCN solutions of methanol (DPEL solutions) at 25 °C. Even with rinses

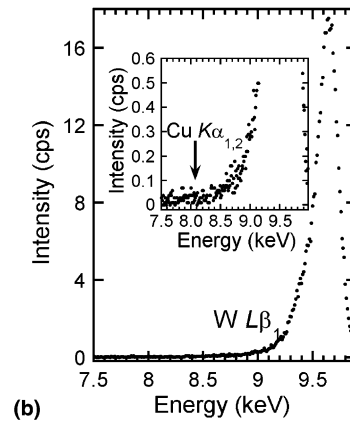
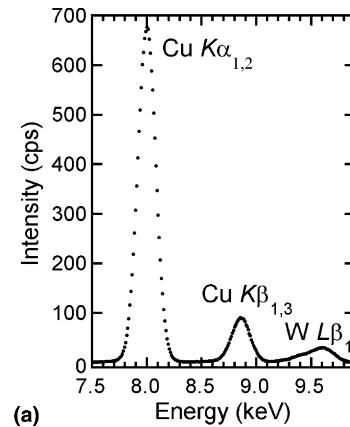


Fig. 1. TXRF spectra of the SiO₂/Si specimens: (a) after immersion in the 0.1 M CuCl₂ solution; (b) after cleaning specimen (a) with the 0.1 M KCN solution of methanol at 25 °C.

in ultra-pure water and methanol, a peak due to CuK α radiation was observed with a high intensity (spectrum a), and the Cu concentration at the SiO₂ surface was estimated to be 2.4×10^{14} atoms/cm² (cf. Table 1). When the Cu-contaminated specimens were cleaned with the DPEL cleaning solutions at 25 °C, no peak due to CuK α radiation was observed, indicating that the Cu concentration decreased below the detection limit of the TXRF spectrometer (i.e., $\sim 3 \times 10^9$ atoms/cm²) (first row in Table 1). After the SiO₂/Si specimens with the Cu contaminants were cleaned with a 0.5% DHF solutions, a peak due to CuK α radiation was observed and the residual Cu concentration

Table 1
Surface Cu concentrations determined from the TXRF measurements

| Specimens | Cleaning solutions | Cu concentration | |
|----------------------|--|--|---|
| | | Before cleaning (atoms/cm ²) | After cleaning (atoms/cm ²) |
| SiO ₂ /Si | 0.1 M KCN of methanol | 2.4×10^{14} | Below 3×10^9 |
| Si | 0.1 M KCN of methanol | 1.4×10^{14} | Below 3×10^9 |
| SiO ₂ /Si | 0.1 M KCN of methanol with 1 mM Cu ²⁺ | 2.4×10^{14} | Below 3×10^9 |
| SiO ₂ /Si | 0.25 M (0.5%) HF aqueous solution | 6.0×10^{14} | 1.4×10^{10} |

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