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Full Length Article

Chemical state analysis of heavily phosphorus-doped epitaxial silicon films grown on Si (100) by X-ray photoelectron spectroscopy

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ABSTRACT

In this work, we investigated the chemical bonding states in highly P-doped Si thin films epitaxially grown on Si (001) substrates using high-resolution X-ray photoelectron spectroscopy (HR-XPS). HR-XPS P 2p core-level spectra clearly show spin-orbital splitting between P $2p_{1/2}$ and P $2p_{3/2}$ peaks in Si films doped with a high concentration of P. Moreover, the intensities of P $2p_{1/2}$ and P $2p_{3/2}$ peaks for P-doped Si films increase with P concentrations, while their binding energies remained almost identical. These results indicate that more P atoms are incorporated into the substitutional sites of the Si lattice with the increase of P concentrations. In order to identify the chemical states of P-doped Si films shown in XPS Si 2p spectra, the spectra of bulk Si were subtracted from those of Si:P samples, which enables us to clearly identify the new chemical state related to Si—P bonds. We observed that the presence of the two well-resolved new peaks only for the Si:P samples at the binding energy higher than those of a Si—Si bond, which is due to the strong electronegativity of P than that of Si. Experimental findings in this study using XPS open up new doors for evaluating the chemical states of P-doped Si materials in fundamental researches as well as in industrial applications.

1. Introduction

As conventional scaling-down technology is facing physical limitations, strain engineering technologies by forming the epitaxial layers with different lattice parameters from Si in the source/drain (S/D) region have been intensively studied for advanced complementary metal-oxide-semiconductor (CMOS) devices. For example, $Si_{1-x}Ge_x$ has widely employed as a stressor in the S/D region to induce compressive strain in the channel region for p-type metal-oxide-semiconductor field-effect transistors (pMOSFETs) [1,2]. In comparison, for the n-type metal-oxide semiconductor field-effect transistors (nMOSFETs), $Si_{1-x}C_x$ alloy has been investigated to enhance device performances, but its contact resistance is not low enough to meet requirement for down-scaled devices [3–5]. Recently, in situ-phosphorus-doped (ISPD) epitaxial Si films have attracted considerable attention as S/D materials for the nMOSFETs, due to their low contact resistance as well as strain generating characteristics [6–9]. In addition to the electronic device applications, the syntheses of highly P-doped epitaxial Si in the form of silicon nanocrystals (Si NCs) and quantum dots (QDs) has also been actively researched for the optoelectronic, photonic, and photovoltaic applications due to their novel electronic and optoelectronic properties [10,11].

For the MOSFET and optoelectronic device applications, it is crucial to precisely analyze the chemical bonding states of P-doped Si materials because the changes in the atomic bonding and their oxidation states have a significant impact on electrical and optical properties. Numerous X-ray photoelectron spectroscopy (XPS) studies have been performed to characterize the effects of the addition of phosphorus on the chemical bonding states in the Si-based materials. Initially, P—O and P—Si chemical states were confirmed in the XPS results using phosphorus ion-implanted Si wafer and P_2O_5 powder, respectively [12]. P dopant distributions and their chemical states for P-doped Si, P-doped poly-Si, and undoped poly-Si have been reported [13–16]. Furthermore, chemical analyses have been conducted on P-doped Si nanocrystals in order to examine the modification of the electrical and photoluminescence properties by P doping in Si NCs [11,17–19]. Considering the importance of P-doped Si materials for both the scientific as well as technological aspects, it is necessary to further understand the fundamental properties of chemical and electronic structures of P-doped Si materials, comparing them to the well-known characteristics of SiO_2 and Si [20,21].

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To the best of our knowledge, however, no experiments have confirmed the chemical bonding states with HR-XPS core-level spectra in P-doped Si thin films. Furthermore, no quantitative study has combined a qualitative identification of chemical states upon the incorporation of P into Si lattices. The reasons why comprehensive XPS results have not yet been reported are as follows: (1) It has been difficult to grow high quality epitaxial Si films doped with high P concentrations at a low temperature due to such difficulties as the strong surface segregation and low solubility of P in Si [13,15,16,22–25]. (2) Even if a high concentration Si:P layer is formed using the implantation process, an additional heat treatment process for lattice curing must be employed, which decreases the P concentration due to the P diffusion and thus prevents the observation of the splitting between P $2p_{1/2}$ and P $2p_{3/2}$ peaks observed in the regime of high P concentrations [12,14,17,26]. (3) XPS measurement technology was not fully developed to detect the fine splitting due to the overlapping of measured spectra. This strong motivation has led to the comprehensive investigation of Si thin films doped with different concentrations of P in terms of qualitative identification and quantitative description of the changes in chemical states upon the incorporation of P into Si lattices.

In this study, we examine the chemical bond states of P-doped Si films as a function of P concentrations using XPS. To understand the effects of P doping on chemical states, survey and core-level (P 2s, P 2p, Si 2s, Si 2p, O 1s, and C 1s) XPS spectra were recorded and fitted into well-resolved contributions. The binding energy and intensity of peaks were quantitatively analyzed as a function of P concentrations. We found that P 2p spectra have revealed the nature of the Si—P bond in Si:P thin films epitaxially grown on Si (001) substrates, which proved in close agreement with the published XRD results. Similar to P 2p spectra, the impact on the chemical states of incorporating P into Si lattices was thoroughly investigated using Si 2p core-level spectra, which produced a new chemical state observed in P-doped samples and related to the Si—P bond. These findings can be interpreted as evidence for the incorporation of P into Si lattices and the dependency of the number of Si—P bonds on the P concentration. This work will shed new light on the understanding of chemical bonding information of P-doped Si materials such as thin films and nanocrystals for device applications as well as fundamental chemical studies.

2. Experimental section

The in situ phosphorus-doped epitaxial silicon films used in this study were grown by a reduced pressure chemical vapor deposition (RPCVD) at 700 °C using dichlorosilane (DCS) and phosphine (PH_3) gases for the Si and P sources, respectively. Before deposition, all samples were dipped in a dilute HF solution (1%) for 1 min to remove any native oxides. The microstructure and thickness of the epitaxial Si:P films grown on Si (001) substrates were examined using high resolution transmission electron microscopy (HR-TEM, JEOL-2100F) at 200 keV. Secondary ion mass spectroscopy (SIMS) measurements were performed by a CAMECA IMS 7f magnetic sector instrument to characterize the phosphorus concentration depth profile in the P-doped Si thin films. Cs^+ primary ions were accelerated at 6 keV with a current of 25 nA. The signal of the $31P^-$ secondary ions was collected to investigate the dopant distribution within the Si:P films. In order to identify the chemical bond states of heavily P-doped Si thin films and bulk Si, near-normal angle XPS measurements were carried out with a K-alpha (Thermo Scientific) XPS system using monochromated Al Kα X-rays ($h\nu = 1486.6$ eV). The concentric hemispherical analyzer was operated at a pass energy window of 200 eV and 40 eV for the fast wide-scan mode (XPS survey) and XPS core-level mode, respectively. The energy resolution of the instrument at 40 eV is 0.5 eV, which is estimated from the full width at half maximum (FWHM) of the XPS Ag $3d_{5/2}$ spectra. The base pressure of the analysis chamber was below 5×10^{-7} Pa and the spot size of the X-ray probe was 300 μm in diameter. No extra XPS signals were detected within the sensitivity of the XPS measurements except those from chemical elements that make up the chemical composition of P-doped Si thin films and bulk Si. Survey and core-level (P 2s, P 2p, Si 2s, Si 2p, O 1s, and C 1s) XPS spectra of P-doped Si thin films and bulk Si were obtained. The binding energies were calibrated by assigning the main Si 2p peak at 99.4 eV [27,28], because the signal of the C 1s peak from our samples is lower than that of the Si and P peaks. All the binding energies in this work were precisely determined within ±0.2 eV using an XPS handbook [27]. To precisely identify the chemical bond states of spin-orbit doublet peaks in P 2p and Si 2p core-level spectra, peak fitting was performed using Shirley background subtraction and Gaussian-Lorentzian functions [29].

3. Results and discussions

Fig. 1(a)–(c) are cross-sectional transmission electron microscopy (TEM) images of as-deposited Si:P layers with a high P-concentration of 6.2% on a Si (001) substrate. The low magnification image in Fig. 1(a) displays a 60-nm-thick uniform Si:P layer on Si substrate without any trace of defects in such a highly P-doped layer, which is more clearly demonstrated in the high resolution images of the films at the surface or at the interface with the Si substrate, as shown in Fig. 1(b) and (c). In order to precisely measure the P-concentration in the Si:P films, we analyzed the samples with different P concentrations using secondary ion mass spectroscopy (SIMS), of which results are shown in Fig. 1(d). The profiles of phosphorus atoms in Si:P film show the uniform P concentration as high as 3.1×10^{21} atoms/cm^3 (about 6.2%) throughout the 60-nm-thick films. Similar to the 6.2% P-doped sample in Fig. 1, other Si:P samples did not show any defects in the TEM images (not shown here).

Fig. 2 presents the full-range XPS spectra of epitaxially grown Si films with P-contents between 0.6% and 6.2% as well as epitaxial Si films without P-doping and bulk Si wafers. The fast wide-scan XPS survey spectra demonstrate core-level peaks of P 2s, P 2p, Si 2s, Si 2p, O 1s, and C 1s. In order to precisely analyze the chemical bonding of the Si:P layers, all peak positions are calibrated to the main Si 2p peak, which was assigned at 99.4 eV. In the spectra, it is clearly noted that a dominant XPS P 2p peak is present near 129 eV in the heavily P-doped Si films (P above 3.5%), while all the samples produce almost identical peaks of Si 2s, Si 2p, O 1s, and C 1s.

To examine the chemical characteristics of P 2p bonding in the P-doped films, we checked the HR-XPS P 2p core-level spectra for the Si:P samples with various P concentrations. For the reference cases without P-doping, we prepare epitaxial Si-films on Si (100) substrates as well as bulk (100) Si wafers. Fig. 3(a) clearly shows spin-orbital splitting between P $2p_{1/2}$ and P $2p_{3/2}$ peaks in P 2p core-level spectra without any curve fitting in P-doped Si films of the P-contents of 3.5% and more. For a quantitative understanding, the curve fitting of P 2p spectra was performed using Gaussian-Lorentzian fitting after a Shirley-type background subtraction. The XPS P 2p spectra are fitted into three well-resolved contributions (plasmon loss peak of the Si 2p, P $2p_{1/2}$, and P $2p_{3/2}$), as depicted in Fig. 3(d)–(f). The detailed XPS parameters in these spectra are given in Table 1.

Two peaks near 129.9 and 129.0 eV appeared in the XPS P 2p core-level spectra in all Si:P samples with the P-content values over 3.5%. They were assigned to the P $2p_{1/2}$ and P $2p_{3/2}$ peaks, respectively [27,28]. Moreover, these two corresponding peaks