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The Schottky barrier of Co on strained and unstrained Si_xGe_{1-x} alloys

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Abstract

In this study, metal films of Co were deposited in situ on strained and unstrained Si_xGe_{1-x} alloys, and the Schottky barrier ($E_F - E_V$) was determined by angle resolved ultraviolet photoemission spectroscopy (ARUPS). Measurements were obtained as a function of Ge composition. Strained and unstrained epitaxial Si_xGe_{1-x} alloys were grown on Si(100) wafers using electron beam evaporation in an ultra-high vacuum molecular beam epitaxy (UHV MBE) chamber. The ARUPS experiments were performed to measure the Schottky barrier heights of Co on a series of Si_xGe_{1-x} alloys, and to observe the surface states. The surface states of clean Si_xGe_{1-x} alloys were observed and were extinguished as Co thickness increased to ~ 0.4 Å. The p-type Schottky barrier of Co on Si was found to be 0.52 eV. The measured barrier heights of Co on strained Si_xGe_{1-x} alloys ranged from 0.33 eV to 0.46 eV as x increased from 0.40 to 0.80. The Schottky barrier of Co on unstrained Si_xGe_{1-x} alloys ranged from 0.23 eV to 0.41 eV as x increased from 0 to 0.60. In fact, the p-type Schottky barrier was essentially identical for strained and unstrained Si_xGe_{1-x} alloys of the same concentration. This indicates that the n-type Schottky barrier is substantially different for strained and unstrained alloys. ARUPS was also conducted to measure the electron affinities of the series of Si_xGe_{1-x} alloys and the work function of Co. The results show that the barrier does not follow the work function model.

1. Introduction

Recently, there has been interest in Si_xGe_{1-x} alloys because of the potential applications in high-speed heterojunction devices [1–5] and in optoelectronics [6,7]. Metal/Si_xGe_{1-x} contacts, however, have not been investigated extensively despite of the importance for device applications. Silicon and germanium are completely miscible over the entire compositional range and give rise to alloys with the diamond crystal structure. Due to the lattice mismatch (4.17%) between silicon and germanium, two types of epitaxial growth of Si_xGe_{1-x} alloys are possible on a bulk substrate, usually Si; strained or pseudomorphic, and unstrained or relaxed. The band gap of the Si_xGe_{1-x} alloys decreases as the Ge content increases, and the strained Si_xGe_{1-x} alloys exhibit a greater reduction in the band gap than unstrained Si_xGe_{1-x} alloy [8]. To date, several attempts have been made to investigate the Schottky barrier of metals on Si_xGe_{1-x} alloys. Kanaya et al. [9] studied the Schottky barrier heights of Pt(Pd)

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silicide/p-Si_xGe_{1-x} using I–V techniques and found that the Schottky barrier heights decrease as the Ge content increases and that the Schottky barrier height of the strained Si_xGe_{1-x} sample is smaller than that of the relaxed one. Liou et al. [10] also performed an experiment about the interfacial reactions and Schottky barriers of Pt/n-$Si_{0.8}Ge_{0.2}$ and Pd/n-$Si_{0.8}Ge_{0.2}$ with I–V measurements. They found that the Schottky barrier heights are much smaller than those of n-Si.

In this work, the Schottky barrier heights of cobalt (Co) on Si, strained Si_xGe_{1-x} alloys ($x = 0.40$, 0.60, and 0.80) and unstrained Si_xGe_{1-x} alloys ($x = 0$, 0.20, 0.40, and 0.60) were measured using angle resolved ultraviolet photoemission spectroscopy (ARUPS). With this technique, the barrier height not only can be measured for a submonolayer film but also can be directly deduced by determining the valence band edge and the Fermi level position. Surface reconstruction and contamination were monitored by means of in situ low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The purpose of this study is to examine the Schottky barrier heights of Co on a series of Si_xGe_{1-x} alloys as a function of Ge composition and the effects of strained and unstrained Si_xGe_{1-x} alloys on the Schottky barrier heights. The Schottky barrier formation will also be discussed in comparison with existing models.

2. Experimental procedures

The samples were prepared and measured using an integrated ultra-high vacuum (UHV) system, which consists of molecular beam epitaxy (MBE), ARUPS, LEED, AES, and loadlock chambers linked by a UHV transfer line. The Si_xGe_{1-x} film growth, the Co deposition and the surface measurements were all made in UHV without exposure to ambient.

The substrates used in this study were 25 mm diameter n-type Si(100) wafers with a resistivity of 0.8–1.2 Ω cm. The wafers were cleaned by exposure to UV/ozone for 5 min to remove hydrocarbon contaminants, an HF based spin etch ($HF:H_2O$:ethanol = 1 : 1 : 10) to remove the native oxide, and followed by in situ heat cleaning to 850°C for 10 min in the UHV MBE chamber to eliminate the residual contamination. The wafers were mounted with tantalum (Ta) wire on a molybdenum (Mo) sample holder. A 200 Å homoepitaxial silicon buffer layer was deposited on the atomically clean Si(100) substrate to ensure a contamination free interface. A series of Si_xGe_{1-x} alloys were epitaxially grown on top of the silicon buffer layers using electron beam evaporation in the UHV MBE chamber. The base pressure of the MBE chamber was better than 1×10^{-10} Torr. The substrate temperature was held at 550°C during all depositions. The parameters of samples used in this experiment were 300 Å for pure Si and pure Ge, and 200 Å, 120 Å, and 40 Å, which are far below the critical thicknesses [11], for strained $Si_{0.8}Ge_{0.2}$, $Si_{0.6}Ge_{0.4}$ and $Si_{0.4}Ge_{0.6}$ alloys, respectively. For unstrained $Si_{0.6}Ge_{0.4}$, $Si_{0.4}Ge_{0.6}$, and $Si_{0.2}Ge_{0.8}$ samples, 8000 Å, 5000 Å, and 3000 Å were chosen respectively, which are far above the critical thicknesses [11]. LEED images of these samples exhibited a sharp double domain 2×1 surface reconstruction, and AES data indicated no detectable carbon or oxygen on the surface before or after Si_xGe_{1-x} alloy depositions. The Co was evaporated at a rate ~ 0.05 Å/s using a tungsten filament under a pressure in the 10^{-9} Torr with the sample kept at room temperature in the UHV ARUPS chamber. The thickness of the Co layer was monitored by a quartz oscillator.

ARUPS was employed to measure the Schottky barrier heights and to observe the surface states of the clean surface. The base pressure of the ARUPS chamber was less than 2×10^{-10} Torr with an operating pressure of $< 1 \times 10^{-9}$ Torr. The ARUPS spectra were obtained with a differentially pumped He discharge lamp delivering the HeI (21.2 eV) radiation. The UV light is incident on the sample at ~ 45° from the surface normal in the analyzer rotation plane and at ~ 15° from the surface in the perpendicular plane to the analyzer rotation plane. The photoemitted electrons were analyzed with a 50 mm mean radius hemispherical analyzer with an energy resolution of 0.25 eV and an angular resolution of 2°. The analyzer is mounted on a two stage goniometer which allows angle dependent measurement and can be rotated in the plane which is perpendicular to the surface of the sample. All ARUPS experiments presented in this paper were performed at emission angles, Θ_e, along the [010]

crystal direction, since along the [010] direction, the surface Brillouin zones of the two domains are equivalent according to the crystal symmetry. The selection of angle for comparison in the spectra was chosen to emphasize features associated with the bulk states of Si, Ge, or Si_xGe_{1-x} alloys. Each spectrum was acquired using a 0.005 eV step size and an integration time of 1 s at each energy. To improve the signal-to-noise ratio, each sample was scanned five times and the five spectra were summed. After summing, the spectra were subjected to a five point smooth to further distinguish the data from the random noise. The position of the Fermi level was determined by measuring either a spectrum of a thick Co layer on the semiconductor or a spectrum of the metallic (Mo) sample holder. Both techniques yielded the same values.

3. Results and discussion

The Schottky barrier height of a metal on a p-type semiconductor is defined as the energy difference between the valence band edge of the semiconductor and the Fermi level of the metal at the interface. In order to determine the Schottky barrier height from ARUPS data, it is necessary to establish the position of the valence band edge in the spectra. The valence band position, which is distinguished by the onset of the spectra, can also be expressed relative to the bulk peaks. Experiments are therefore limited to thin metal films because photoemission from the metal overlayer tends to mask that from the underlayer, and it obscures features necessary to determine the valence band edge at higher metal coverage.

An emission angle of 35° was chosen for the pure Si sample and the strained Si_xGe_{1-x} samples, while a 30° emission angle was chosen for the unstrained Si_xGe_{1-x} samples, because the bulk state features are prominent at these angles. ARUPS spectra of Co on the strained $Si_{0.8}Ge_{0.2}$ and the unstrained $Si_{0.2}Ge_{0.8}$ for different Co coverage are shown in Fig. 1 and Fig. 2. The spectra of the clean strained $Si_{0.8}Ge_{0.2}$ at a 35° emission angle and the clean unstrained $Si_{0.2}Ge_{0.8}$ at a 30° emission angle look similar, but there is a substantial difference in the spectra obtained at normal emission for the same samples. The feature (S) associated with the dangling

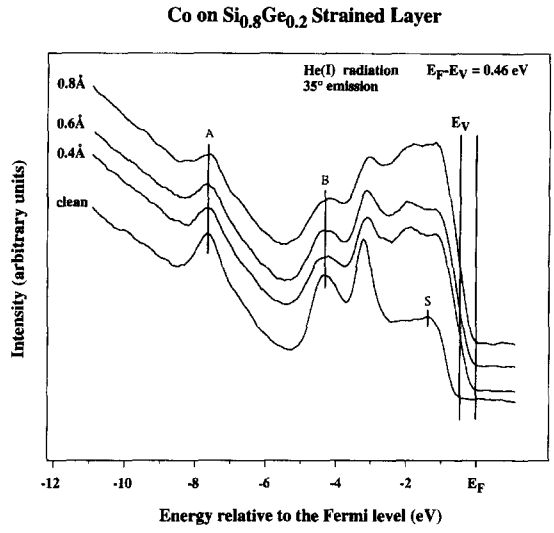

Fig. 1. The ARUPS spectra of clean strained $Si_{0.8}Ge_{0.2}$ alloy, and Co on strained $Si_{0.8}Ge_{0.2}$ alloy obtained as a function of Co coverages. A and B indicate states due to bulk transition and S indicates a surface state attributed to dangling bond states.

bond surface state located at 1.37 eV below the Fermi level was observed from the clean strained $Si_{0.8}Ge_{0.2}$ spectrum and was extinguished with Co evaporation. The features (A, B) due to the bulk transition at 7.64 eV and at 4.33 eV below the Fermi

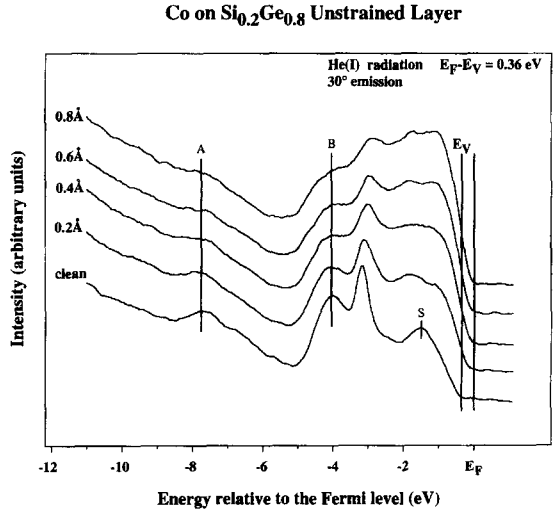

Fig. 2. The ARUPS spectra of clean unstrained $Si_{0.2}Ge_{0.8}$ alloy, and Co on unstrained $Si_{0.2}Ge_{0.8}$ alloy obtained as a function of Co coverages. A and B indicate states due to bulk transition and S indicates a surface state attributed to dangling bond states.

Table 1
The measured Schottky barrier heights ($E_F - E_V$) of Co on Si, strained Si_xGe_{1-x} alloys, and unstrained Si_xGe_{1-x} alloys. The value for Si is also shown in the strained column for comparison

Strained	$E_F - E_V$ (eV)	Unstrained	$E_F - E_V$ (eV)
Si (cubic)	0.52 ± 0.03	Si (cubic)	0.52 ± 0.03
$Si_{0.8}Ge_{0.2}$	0.46 ± 0.03		
$Si_{0.6}Ge_{0.4}$	0.39 ± 0.03	$Si_{0.6}Ge_{0.4}$	0.41 ± 0.03
$Si_{0.4}Ge_{0.6}$	0.33 ± 0.03	$Si_{0.4}Ge_{0.6}$	0.36 ± 0.03
		$Si_{0.2}Ge_{0.8}$	0.36 ± 0.03
		Ge	0.23 ± 0.03

level were used as reference peaks for deducing the valence band edge after Co deposition. The valence band edge, which was found to be 7.18 eV above the reference peak A, was determined by the onset of emission at ~0.46 eV below the Fermi level from the clean $Si_{0.8}Ge_{0.2}$ spectrum. No shifts in the kinetic energies of the peak originating from bulk transition were observed for all measured samples and for all Co coverages. The Schottky barrier height ($E_F - E_V$) of 0.46 eV and 0.36 eV were deduced for Co on the strained $Si_{0.8}Ge_{0.2}$ and the unstrained $Si_{0.2}Ge_{0.8}$, respectively. The measured Schottky barrier heights for all of the samples are summarized in Table 1.

Fig. 3 shows a schematic drawing of the band alignment with the $E_F - E_V$ for the strained Si_xGe_{1-x} alloys with Co overlayer. The band alignment for strained Si_xGe_{1-x} alloys on Si(100) substrates is type I with a band discontinuity of 0.020 eV at the conduction band [12]. The Schottky barrier heights of Co on the series of strained Si_xGe_{1-x} alloys are pinned at around the middle of the band gap.

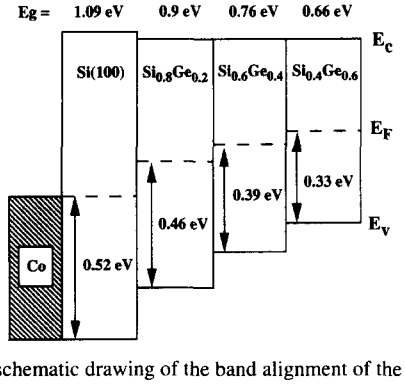

Fig. 3. A schematic drawing of the band alignment of the $E_F - E_V$ for strained Si_xGe_{1-x} alloys with a Co overlayer. The band alignment for strained Si_xGe_{1-x} alloys on a Si(100) substrate is type I [12].

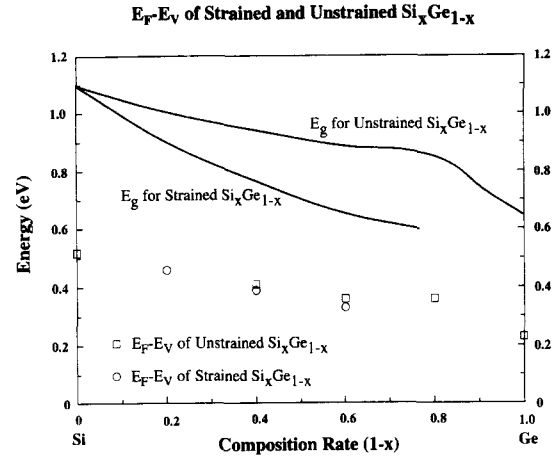

Fig. 4. The p-type Schottky barrier heights of Co on strained and unstrained Si_xGe_{1-x} alloys with the band gap reported by People [8].

The Schottky barrier heights of Co on the strained and the unstrained Si_xGe_{1-x} alloys in Table 1 are plotted in Fig. 4 together with the band gap obtained by People [8]. It is noted that the Schottky barrier height of Co on strained and unstrained Si_xGe_{1-x} alloys decreases with increasing Ge content, which is similar to the results for Pt(Pd) in contact with the Si_xGe_{1-x} alloys obtained by Kanaya et al. [9]. The Schottky barrier heights, however, were identical for Co on strained and unstrained Si_xGe_{1-x} alloys with the same Ge content despite the fact that the strained and unstrained Si_xGe_{1-x} alloys exhibit substantial differences in the band gap for identical alloy concentrations. In other words, the n-type Schottky barrier heights of unstrained Si_xGe_{1-x} alloys are remarkably larger than those of strained Si_xGe_{1-x} alloys since the n-type barrier height can be obtained by subtracting p-type Schottky barrier height from the energy band gap of the semiconductor.

The ARUPS spectra of the alloys were extended to measure the electron affinity of the semiconductor and the work function of metal. The electron affinity of the semiconductor and the metal work function are given by

$\chi = h\nu - D - E_g$ for the electron affinity of the semiconductor, and

$\phi = h\nu - D$ for the metal work function,

where $h\nu$ is the incident energy (21.21 eV for He I radiation), E_g is the band gap of the semiconductor, and D is the width of the ARUPS spectrum. To obtain the width it is necessary to bias the sample to overcome the work function of the analyzer. The Co work function was found to be 4.98 eV which is in close agreement with the reported work function (5 eV) of bulk Co [13]. The measured electron affinities of Si, strained Si_xGe_{1-x} alloys and unstrained Si_xGe_{1-x} alloys ranged from 3.83 eV to 4.05 eV ($\chi_{Si} < \chi_{Ge}$) and showed a slight difference between measured values of the electron affinities of Si and Ge and previously reported values ($\chi_{Si} = 4.01$ eV, $\chi_{Ge} = 4.13$ eV) [14]. The calculated values of the p-type Schottky barrier using the measured electron affinities and the Co work function resulted in negative values for all alloys. This indicates that the Schottky barrier of Co on a series of strained and unstrained Si_xGe_{1-x} alloys is not consistent with the work function model. The results suggest that the Fermi level has been pinned by interface states [15].

4. Conclusions

It was shown that the measured Schottky barrier height of Co on a series of Si_xGe_{1-x} alloys decreased as the Ge content increased. No significant difference, however, was observed between the measured p-type Schottky barrier heights of Co on strained Si_xGe_{1-x} alloys and those of Co on unstrained Si_xGe_{1-x} alloys of the same Ge concentration. Since the band gap of the strained and unstrained alloys are significantly different, this indicates that the n-type barrier differs for the strained and unstrained alloys. It was also shown that the barrier heights of Co on strained Si_xGe_{1-x} alloys and unstrained Si_xGe_{1-x} alloys do not follow the work function model, which suggests that the Fermi level has been pinned by interface states.

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