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A BEEM Study on Effects of Annealing Temperature on Barrier Height Inhomogeneity of $CoSi_2$/Si Contact Formed in Co-Ti-Si Systems*

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Abstract: Ultra-thin epitaxial $CoSi_2$ films are fabricated by solid state reaction of a deposited bilayer of Co(3nm)/Ti(1nm) on n-Si(100) substrates at different temperatures. The local barrier heights of the $CoSi_2$/Si contacts are determined by using the ballistic electron emission microscopy (BEEM) and its spectroscopy (BEES) at low temperature. For $CoSi_2$/Si contact annealed at 800℃, the spatial distribution of barrier heights, which have mean barrier height of 599meV and a standard deviation of 21meV, obeys the Gaussian Function. However, for a sample that is annealed at 700℃, the barrier heights of it are more inhomogenous. Its local barrier heights range from 152meV to 870meV, which implies the large inhomogeneity of the $CoSi_2$ film.

Key words: BEEM; schottky barrier height; silicide; inhomogeneity
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1 Introduction

Barrier heights over a real Schottky metal-semiconductor (M-S) contact are usually imhomogenous due to the local defects, the non-uniformity of the interface charges, the thickness and the composition of the silicide, etc.[1~3] Conventional techniques, such as current-voltage and capacitance-voltage (I-V/C-V) or photo-emission, can only help to determine the average of barrier height over the whole contact. The newly developed technique, ballistic electron emission microscopy (BEEM), based on STM (scanning tunneling microscopy), is very suitable to scan a buried interface under a thin silicide film[4]. Local barrier heights on a nanometer scale can be deduced from the BEEM and its spectroscopy (BEES). Spatial distribution of barrier heights was obtained directly by using BEEM/BEES. For details, please see the paper by Palm et al for Au/Si contacts[5] and see our published papers for $CoSi_2$/Si[6] and PtSi/Si contacts[7]. By using such a distribution, the deviation of the experimental I-V characteristics from the ideal thermionic emission-diffusion (TED) model can be explained[8].

Furthermore, BEEM is also a powerful technique to characterize the electrical and structural properties of a M-S contact in a microscopy view. For example, the milling effects of Ar^+ ion on PtSi/Si and Au/Si contacts were studied by using the measurements of BEEM in our previous paper[9].

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Van Känel et al found that the low barrier height in an epitaxial $CoSi_2$(100) on (100) Si is related to a dislocation[10]. In this paper, ultra-thin $CoSi_2$ films formed by solid state epitaxy on Si(100) at different temperatures are studied by using the BEEM measurement.

2 Experiment

It was ready with a phosphor doped, n-Si (100) wafer with a resistivity of 3~ 5Ω·cm. Active areas of rectangular shape (1mm×4mm) were defined by using the standard process of thermal oxidation, lithography and wet etching. After RCA cleaning and dipping in a diluted HF solution, the wafer in a vacuum chamber of an Oxford sputtering system was loaded with a base pressure of about 1×10^{-4}Pa. 1nm of Ti and 3nm of Co were deposited sequentially by Ar^+ ion beam sputtering without breaking the vacuum. The silicidation was achieved in an ex-situ two-step RTA (rapid thermal annealing) process. The first step of RTA was started in pure N_2 ambient at 550℃, after 60s, the un-reacted metal was removed by a selective etching. Then, the second step of RTA was carried out at 650℃ for 1min, at 700℃ for 1min, at 750℃ for 1min, at 750℃ for 10min, at 800℃ for 10s, and at 800℃ for 1min. At adopting such a process of TIME (Ti-interlayer mediated epitaxy), it is well known that the formed $CoSi_2$ film is epitaxial[11,12].

BEEM measurements were performed in an AIVIB-4B surface/interface system using a Pt-Ir tip in air. Since the barrier height of $CoSi_2$/Si contact is relatively low (about 0.6eV), the BEEM measurements should be carried out at low temperature to suppress the thermal noise. As to our experiments, the apparatus was cooled down in liquid N_2 until about − 50℃ during the measurement. Several hundred locations on the surface of each sample were chosen randomly but keep the distance of any two locations longer than 2nm over the entire contact by BEEM spectra. For each spectrum, the tunnel current I_t was maintained constant at 3.0nA, and the tip voltage (V_t) was varied from − 100mV to − 1100mV in steps of − 10mV. Besides, scans were taken at the same location for 5~ 10 times and the results were averaged in order to improve the ratio of signal to noise.

3 Results and discussion

Annealing temperature is a key parameter for the formation of the $CoSi_2$ films. If the temperature exceeds a critical degree, the sheet resistance of the $CoSi_2$ film will increase dramatically. The thinner $CoSi_2$ film has a lower critical temperature[13]. For our experiment of ultra-thin Co (3nm) on Si, the $CoSi_2$ film began to be destroyed when the annealing temperature exceeds about 800℃. On the contrary, if the temperature is too low, the Co-Si reaction will not be complete. As to our experiments for ultra-thin Co, the annealing temperature of about 600℃ or above is necessary to form the $CoSi_2$ film.

Figure 1 shows a typical BEEM spectrum measured on the sample which was formed by annealing of 800℃/10s. The local barrier height can be determined by using the Kaiser-Bell quadratic

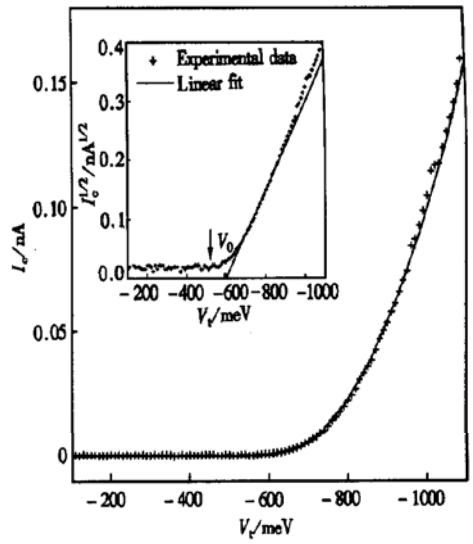


Fig. 1 A typical BEEM spectrum (I_c-V_t) and its quadratic fitting The inset shows the $\sqrt{I_c}$-V_t plot for determination of the local barrier height.

law[4], i. e., the collector current is $I_c = R(V_t - \Phi_b + k_B T)^2$ near the threshold voltage, where Φ_b is the local barrier height, K_B is the Boltzmann constant, T is temperature in Kelvin, R is the transmission factor. Then the plot of $\sqrt{I_c}$-V_t should be a straight line, as shown in the inset of Fig. 1., Φ_b is then determined from the intercept on the voltage axis. 341 points on sample 1 were measured totally and the Φ_b distribution is shown in Fig. 2. A histogram was made by taking the number of counts in an interval of 12.5meV. The experimental distribution with a mean barrier height of 599meV and a standard deviation of 21meV obeys a Gaussian distribution quite well. However, the linearity of the $\sqrt{I_c}$-V_t line (inset of Fig. 1) is not exactly linear due to factors such as scattering, electrical broadening of the Fermi level and the noise. This will result in the experimental error for the Φ_b and broaden the Φ_b distribution[14]. By measuring several BEEM spectra at the same location, we found that the uncertainty of the BEEM measurement is smaller than the variation of Φ_b at different locations. It implies that the deviation of the distribution in Fig. 2 is mainly caused by the difference of Φ_b itself. Furthermore, there are two points with a very low barrier height (about 370meV) in Fig. 2. These low Φ_b patches may be corresponded to defects in the $CoSi_2$ film.

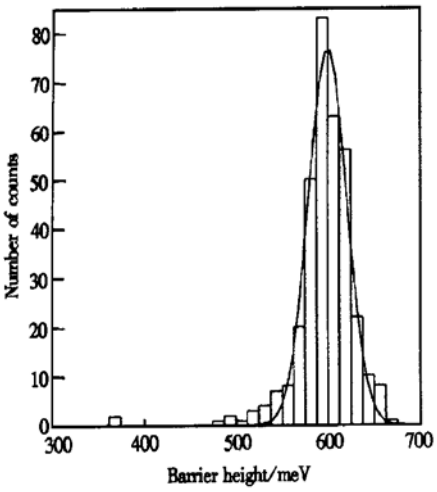


Fig. 2 Statistical barrier height distribution and its Gaussian fitting for the annealed $CoSi_2$/Si contact at 800℃

The other $CoSi_2$/Si contacts were also measured by BEEM. We found that the BEEM signals for the samples at lower annealing temperature were not as stable as that for the samples at 800℃. Since a lot of BEEM spectra are necessary for statistical analysis, it is time-consuming. Thus only one sample, which was formed at annealing temperature of 700℃ for 1min, was measured in details. The Φ_b distribution of this sample is shown in Fig. 3. 347 points on this sample were measured totally. The distribution is significantly different from that of the sample annealed at 800℃. The barrier heights range from 152meV to 870meV. The most part of the Φ_b is at about 600meV with the mean barrier height of 579meV and the standard deviation of 58meV. This can be fitted by a Gaussian function. Figure 4(a) and (b) show a typical BEEM spectra with low barrier height and with high barrier height on this sample respectively. The quadratic law was also used to determine the value of Φ_b. It should be noted that the strength of BEEM current in low Φ_b patch is much bigger than that of the normal BEEM current (as shown in Fig. 1) while the strength of BEEM current in high Φ_b position is much smaller than the

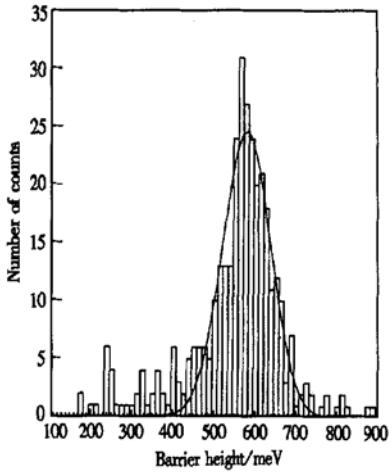
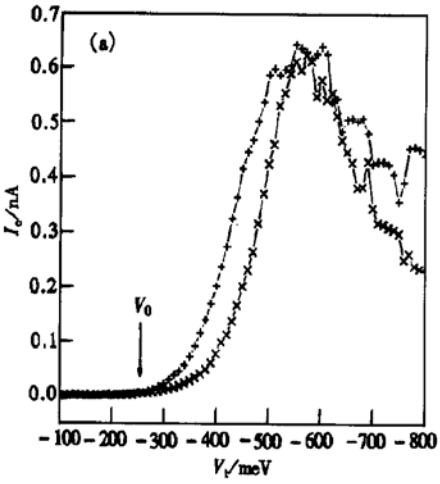


Fig. 3 Statistical barrier height distribution and its Gaussian fitting for the annealed $CoSi_2$/Si contact at 700℃

normal strength.



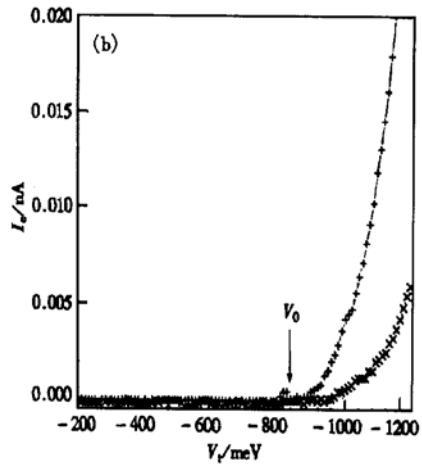


Fig. 4 Two typical BEEM spectra (I_c-V_t) measured at (a) low barrier height locations and (b) high barrier height locations on the annealed $CoSi_2$/Si contact at 700℃

According to the pinch-off model[1], the barrier height drop around a small low Φ_b patch displays a smaller value than its actual one, and the apparent Φ_b value depends on the patch area. The low value of Φ_b points measured in this sample may be related to the pinhole or to the uncontinuity of the $CoSi_2$ film[11]. The different barrier heights at those points maybe measured at different area of the pinhole. This also explains that the strong BEEM current occurs through those low points of Φ_b.

On the other hand, the high Φ_b points may be due to the remaining of Co(Ti)Si_x alloys or the Co oxide in the $CoSi_2$/Si interface. Electrons emitted from the tip should transport through this layer to be collected, so that the transmission factor is reduced significantly and the threshold value shifts to the direction of high tip voltage. Moreover, local contamination in the $CoSi_2$ surface may also decrease the transmission factor. Since the BEEM current is affected by many other factors[14], quantitative analysis of the transmission factor is difficult.

Above samples were also measured by conventional I-V/C-V methods. Due to the ultra-thin thickness of the $CoSi_2$ film, the Schottky diode has a very large series resistance, which makes it difficult to deduce the meaningful SBH from the I-V or C-V curves. In literature, the barrier height deduced from the I-V/C-V for thin $CoSi_2$/Si film contacts is about 0.60eV[15], which is in agreement with the mean barrier height deduced from the BEEM in this paper.

4 Conclusion

Significant difference in the barrier height distribution for two-type of $CoSi_2$/Si contacts was derived from BEEM measurements at low temperature. It implies that the uniformity of the annealed $CoSi_2$ film at 800℃ is much better than that of the annealed sample at 700℃. It is in agreement with the expectation from the mechanism of solid state reaction of the Co-Ti-Si system[11]. BEEM may be used as a powerful characterization technique for various ultra-thin silicide films.

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用弹道电子显微术研究 Co-Ti-Si 系统的退火温度对 $CoSi_2$/Si 势垒不均匀性的影响*

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摘要: 通过在硅(100)衬底上淀积的 Co(3nm)/Ti(1nm)双金属层在不同退火温度下的固相反应, 在硅衬底上制备了超薄外延 $CoSi_2$ 薄膜. 在低温下, 用弹道电子显微术(BEEM)及其谱线(BEES)测量了 $CoSi_2$/Si 接触的局域肖特基势垒高度. 对于 800℃退火的 $CoSi_2$/Si 接触, 势垒高度的空间分布基本符合高斯分布, 其峰值在 599meV, 标准偏差为 21meV. 而对于 700℃退火样品, 势垒高度分布很不均匀, 局域的势垒高度值分布在 152meV 到 870meV 之间, 这可归因于 $CoSi_2$ 薄膜本身的不均匀性.

关键词: 弹道电子显微术; 肖特基势垒高度; 硅化物; 不均匀性

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