Thin film characterisation of chromium disilicide

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ABSTRACT

The ambiguous binding energy (BE) shift of the Cr $2p_{3/2}$ peak of chromium disilicide with respect to the one of pure Cr metal in the X-ray photoelectron spectroscopy (XPS) has meant difficulties in practice for silicide determination. In the present study, with the aid of an interconnected ultrahigh vacuum (UHV) system for silicide fabrication and characterisation, high purity Cr–Si thin films with thickness around 100 nm and well-controlled chemistry were produced. The characteristics with respect to chemical composition and phase identity were determined by means of XPS and X-ray diffraction (XRD). The experimental results were also compared with predictions using thermodynamic effective heat of formation (EHF) model. Whilst the BE positions of the core-level Cr $2p_{3/2}$ peak of Cr and CrSi$_2$ are close to each other, larger shifts are determined for their corresponding $L_3M_{23}M_{23}$ Auger transitions. By establishing a chemical-state plot, or the so-called Wagner plot, it is illustrated that the core-level shift caused by the initial-state effects is basically compensated by the one owing to the final-state effects, resulting in a small negative BE shift of the Cr $2p_{3/2}$ peak from metallic state to disilicide state. The valence band spectra were also investigated and correlated to the core-level spectra.

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1. Introduction

Chromium silicide (Cr–Si compounds), especially chromium disilicide (CrSi$_2$), is one of the widely used transition metal silicide materials in microelectronic, thermoelectronic, photovoltaic and optoelectronic devices for its high electrical conductivity and good optical properties [1–7]. In an earlier study [8], authors conducted a characterisation study on different transition metal silicide thin films based on the systems Ti–Si, Fe–Si, Ni–Si and Cr–Si. Whilst pure single silicide phases were prepared in the first 3 systems, the ambiguous double-phase mixture of CrSi and CrSi$_2$ was developed in the last one. To complete the study, further investigation about this particular system has been performed and results are reported here.

In accordance with some XPS studies of chromium silicides [1,2,5], the inconsistency of the reported XPS data has failed to provide a piece of consolidating information about silicide formation, or more specifically, to reveal the type of silicide, by studying the core-level binding energy (BE) position alone [8]. Some possible reasons could be that: the characterisations were conducted on the ion sputter-cleaned surfaces, thus the ordinary chemical state was modified; or, the lack of structural analyses by means of XRD or transmission electron microscopy (TEM). Considering the first issue, we have taken a special precaution here by using an interconnected UHV system to conduct both thin film fabrication and surface characterisation, i.e. ion-beam sputter deposition and XPS analysis, respectively. By this means,

the chances of moisture reaction and atmospheric contamination are minimised, and ion sputter-cleaning before XPS analysis becomes unnecessary. Hence, higher thin film purity, better cleanliness and more reliable XPS results are guaranteed. Considering the second issue, phase identifications of the present synthesised silicide films are determined by means of XRD measurements. Hence, a consistent and clear picture about the synthesised films can be captured. In the present XPS study, Cr silicidation is characterised by taking all XPS core-level emissions, X-ray induced Auger transitions and valence bands into account.

2. Experimental procedures and analysing approaches

Preparation and XPS characterisation of the transition metal silicide thin films were carried out in an interconnected UHV system consisting of a deposition chamber, a vacuum furnace and an XPS instrument at a vacuum level better than 10^{-6} Pa [8]. The binary component thin films with thickness around 100 nm were deposited onto the ion sputter-cleaned Si wafer square pieces in the size of 10 mm × 10 mm. The deposition technology used was ion beam sputter co-deposition method. In this technology, high purity element targets were bombarded by two individually monitored argon ion beams generated by Kaufman-type ion sources, and then the sputtered-out atoms were deposited onto the substrate surface as thin films. Table 1 summarises the sputtering parameters, the co-deposited compositions by XPS quantitative analyses and the corresponding annealing conditions in the UHV furnace.

Specimens were transferred to XPS for chemical analyses before and after annealing. The instrument used was a PHI 5500 X-ray photoelectron spectrometer equipped with a monochromatic AlKα source

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Table 1
Sputtering parameters, co-deposited compositions and annealing conditions of individual Cr–Si specimen.

No.	I_{Cr} (mA)	V_{Cr} (V)	I_{Si} (mA)	V_{Si} (V)	As-deposited composition	Annealing temperature and time
1	20	500	0	0	Cr	No heat treatment
2	12	300	20	500	$Cr_{0.28}Si_{0.72}$	450 °C, 1.50 h
3	10	250	20	500	$Cr_{0.23}Si_{0.77}$	450 °C, 1.25 h
4	8	200	20	500	$Cr_{0.20}Si_{0.80}$	650 °C, 1.00 h

($h\upsilon = 1486.6$ eV) and was calibrated according to the ISO 15472:2001 standard in which the binding energy (BE) spectrum was aligned with the Au $4f_{7/2}$, Ag $3d_{5/2}$ and Cu $2p_{3/2}$ spectral peaks at 83.96 eV, 368.21 eV and 932.62 eV, respectively [9]. The absolute energy resolution of a spectral peak, determined by measuring the full-width at half maximum (FWHM) of the core-level Ag $5d_{5/2}$ peak from a ion sputter-cleaned silver sample, was 0.80 eV with pass energy set at 23.5 eV (for the Cr $2p_{3/2}$ measurements) and 0.60 eV with pass energy at 5.85 eV (for the Si $2p_{3/2}$ measurements). The smallest identifiable energy shift of the peak position is 0.10 eV. The recorded XPS peaks were curve-fitted in the PHI Multipak software by applying Shirley background and asymmetric Gaussian–Lorentzian sum function (Gauss: 80%). The peak intensities of individual chemical state were normalised by the atomic sensitivity factors (ASF) in the quantitative analyses of the thin films compositions, as in [8,10]. For all the measurements, the take-off angle of the photoelectron emission (θ) was 45° and the XPS information depths (d) of chromium and silicon signals in the chromium silicides given by the expression ($d = 3 \cdot \lambda \cdot \sin\theta$) are estimated to be 3.5 nm and 5.4 nm, respectively, using the empirical relation of electron attenuation depth by Seah and Dench [11]; the same estimation for Cr thin film is 2.0 nm.

The phases corresponding to the surface chemical compositions determined by the XPS core-level spectra were confirmed by means of diffractometry using grazing incidence X-ray diffraction (GIXRD) setup in the Bruker D8 Advance X-ray diffractometer equipped with a Cr source (λ = 2.2897 Å). High resolution diffractograms of silicide films were obtained from 40 to 80° at a low scanning rate (i.e. 20 s per step, 0.02° in step) with an incident angle set at 2.0°. The estimated analysing depth of the silicide materials is around 1.1 μm. The diffracted peaks appeared on the diffractograms were matched with the International Centre of Diffraction Data (ICDD) powder diffraction files (PDF-2) in order to identify the phase(s). The identified phases of the thin films after annealing were compared with those predicted by the Pretorius' effective heat of formation (EHF) model [12]. This model determines the thermodynamically favoured phases by comparing the effective heat of formation (ΔH′) of all possible silicide phases in a specific silicide system by using the as-deposited composition as the effective concentration in the following equation:

$$\Delta H' = \Delta H° \times \frac{\text{Effective concentration of limiting element}}{\text{Compound concentration of limiting element}}. \qquad (1)$$

The model assumes that the entropy effects can be neglected, whereby only the effective heat of formation (H) is considered. According to the model, the first formed phase should have the lowest ΔH′ among all possible phases in the binary system and it should be a congruent phase. Generally, non-congruent phase has difficulty to nucleate and is usually disregarded as the first-formed phase, unless the temperature difference between the liquidus curve and the peritectic/peritectoid point is very small in the corresponding phase diagram. Surplus of the needed element can also facilitate this non-congruent phase formation in the subsequent process [12].

3. Results and discussion

3.1. Structural and phase characterisation

A typical diffractogram acquired either from Specimens 2 or 3 after annealing is illustrated in Fig. 1. According to the phase identification, the corresponding diffracted peaks match with the hexagonal $CrSi_2$ phase (PDF: 65-3546). The formation of $CrSi_2$ phase is independent to the initial composition (Table 1) as long as the Cr content is around 20 to 30 at.% and annealed at 450 °C. By increasing the annealing temperature to 650 °C, a double-phase $CrSi$–$CrSi_2$ mixture has been reported (Specimen 4) [8]. Meanwhile, that film was spall off from the substrate. Thus, this temperature would not be an appropriate annealing condition for single-phase chromium disilicide preparation. Conversely, no peak has been acquired from the co-deposited specimens without annealing. Thereby, all thin films are determined to have disordered (amorphous) or short-range ordered (vitreous) structure before annealing [8].

In fact, the formation of $CrSi_2$ in the Cr–Si system can be predicted in a thermodynamic approach by making use of the standard enthalpies of formation (ΔH°) of individual phase in the Cr–Si system. Table 2 shows the individual effective heat of formation (ΔH′) of each possible phase in every specimen evaluated by Eq. (1). For the lowest evaluated ΔH′ among all possible phases, $CrSi_2$ is found to be the common first-formed phase in all the specimens. Then, depending on the availability of Cr, the subsequent phase should be CrSi [12]. The prediction agrees with the XRD results for Specimens 2 and 3, as well as for the double-phase Specimen 4 [8]. However, according to the EHF model, it is precarious to tell the formation of non-congruent CrSi phase after annealing process [8]. For that, we should add that the starting environment of the co-deposited thin films is different from the metal-silicon interface considered in Pretorius' original model [12]. Whilst atomic diffusion (Cr metal in this case) is one governing factor in the phase formation process, Pretorius' concern about the nucleation difficulty of the non-congruent phase along the moving metal–silicon interface actually does not exist in the present study [12]. In fact, the intermixing atoms of co-deposited Cr–Si compounds may have lowered the thermodynamic diffusion barrier and created an optimal environment for monosilicide formation. Therefore, the factor of non-congruency can be neglected. Still, CrSi can only be the subsequent phase once the thermodynamically favoured $CrSi_2$ has formed.

3.2. Chemical state and electronic structure characterisation

In the XPS measurement, BE position of the Cr $2p_{3/2}$ metallic state locates at 574.3 eV. For the co-deposited Cr–Si films, the Cr $2p_{3/2}$ position shifts to 574.0 eV. With reference to Palacio et al., energy provided by
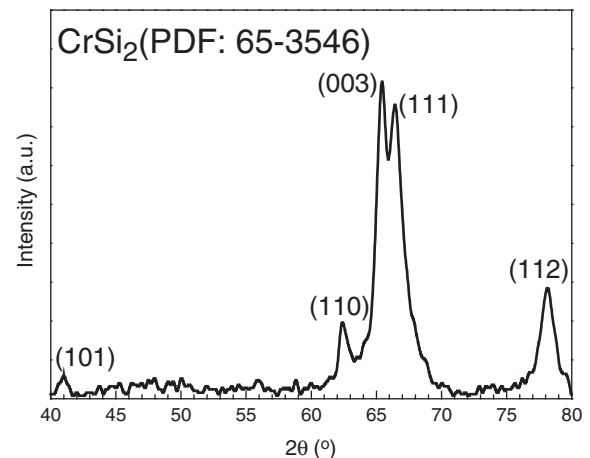

Fig. 1. Diffractogram of $CrSi_2$ thin film after annealing at 450 °C for 1.5 h (Specimen 2).