

An Interpretation of the Shoulder Peaks on the High Energy Resolution N $KL_{23}L_{23}$ Auger Line Shape of TiN extracted by Target Factor Analysis

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Numerically extracted N $KL_{23}L_{23}$ peak shape of TiN has been discussed using a simple model of the electric structure of TiN. Possible Auger transition intensities and energies including hybridized orbitals were proposed and compared with the extracted peak that has been recorded in the high energy resolution mode. The expected peak intensities and energy differences from the model proposed here were basically in good agreement with the N $KL_{23}L_{23}$ peak shape extracted by target factor analysis.

1, Introduction

Titanium nitride is one of the important materials in the fields of semiconductor industry as a diffusion protective film. The properties of this film, a high electric conductivity, high melting point and so on, depend on its chemical composition of nitrogen and titanium. The chemical composition has been determined by Rutherford backscatter spectrometry (RBS)[1], X-ray diffraction (XRD)[2], transmission electron microscopy (TEM)[3] and X-ray photoelectron spectroscopy (XPS)[4].

On the other hand, quantitative analysis of nitrogen and titanium by Auger electron spectroscopy (AES) is well known as a difficult case because of occurring direct overlap of the N $KL_{23}L_{23}$ and Ti $L_{3}M_{23}M_{23}$ Auger peaks in the exactly same energy region, therefore, many researchers have proposed several methods for quantitative compositional analysis by AES[5,6,7,8,9]. In this situation, Watson *et al.* have reported the application of target factor analysis (TFA) on the depth profile data of TiN thin film in order to deconvolute the overlapped N $KL_{23}L_{23}$ and Ti $L_{3}M_{23}M_{23}$ Auger peaks[10].

TFA is an effective data interpretation for multiple data sets of the electron spectra [D] in

order to determine the number of pure components, the target spectra [R] and corresponding weighting factors [C][11]. In this case, the weighting factors that mean the chemical compositions can be verified by other techniques such as a wet chemical analysis. In addition, this is the method proposed by Watson *et al.* that TFA is able to extract the target spectra [R] from the data sets [D] when the weighting factors [C] were substituted. In general, while the extracted target spectra can be verified by measuring the spectra from external standard materials, it is impossible in the case of TiN to verify the shape of the N $KL_{23}L_{23}$ and Ti $L_{3}M_{23}M_{23}$ Auger spectra because of strong overlapping. Watson *et al.* has discussed the similarities of the mathematically extracted peak shape by comparing with the N $KL_{23}L_{23}$ spectrum from HfN. This comparison is one answer for TFA results, however, it is important to discuss more on the mathematically extracted spectral shape whether the extracted Auger spectrum has a physically meaningful(real) shape or not.

In this paper, we discuss the N $KL_{23}L_{23}$ line shape of TiN based on molecular orbital of TiN. Possible combination of the Auger transitions in the hybridized valence electrons, relative Auger intensities and peak positions will be

proposed based on simple model of a linear combination of atomic orbitals (LCAO) of N and Ti atoms. Based on this model, the origin of the shoulder peaks observed in the results of TFA on high-energy resolution data will be assigned.

	Chemical Analysis (atomic %)		
	Ti	N	O
Sample #1	51.0	48.9	0.088
Sample #2	66.6	33.3	0.096
Sample #3	68.4	31.4	0.094

Table 1 The results of chemical composition analysis on three different stoichiometry of Ti and N made by arc ion plating method. These results were applied to TFA to resolve the N KLL and Ti $L_2M_{23}M_{23}$ Auger peaks.

2, Experiment

Three different stoichiometries of TiN_x films were prepared by arc ion plating method on Cu substrates. The amounts of nitrogen were determined by Kjeldahl method and those of titanium were determined by ICP-MS method (table 1). The Auger spectrum on each sample was recorded by Physical Electronics

Inc. ESCA Model 5800 in the energy region of 350 eV to 450 eV in kinetic energy. In addition, high-energy resolution mode (Pass Energy = 23.5 eV) and monochromatized Al K_{α} X-Ray were applied to record the spectra in order to observe the detail of spectral shapes and to avoid the electron damage such as change of the stoichiometry.

3, Results and discussion

Figure 1 shows the results of extracting the N $KL_{23}L_{23}$ and Ti $L_3M_{23}M_{23}$ Auger differential spectra by TFA on the high-energy resolution Auger spectra from TiN_x . Focusing on the peak shape of N $KL_{23}L_{23}$ Auger spectrum, it is seen that there are two shoulder peaks at 383eV and 393eV on the both side of the main peak located at 388eV. In general, the KLL Auger peak of the light elements such as nitrogen, oxygen, or fluorine, these fine structures are not observed in the handbook database [12].

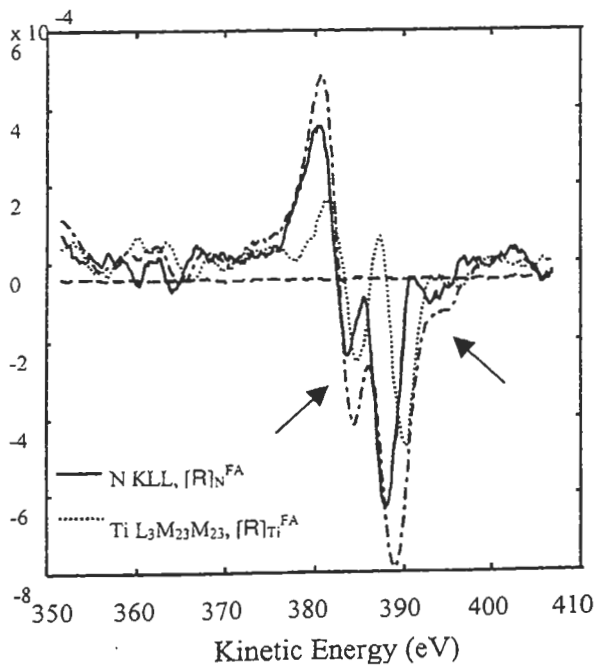


Fig. 1 Results of extracting the N $KL_{23}L_{23}$ and Ti $LM_{23}M_{23}$ spectra by target factor analysis on TiN spectra measured in the high energy resolution mode.

$$\psi_{TiN} = C_N \psi_N + C_{Ti} \psi_{Ti}$$

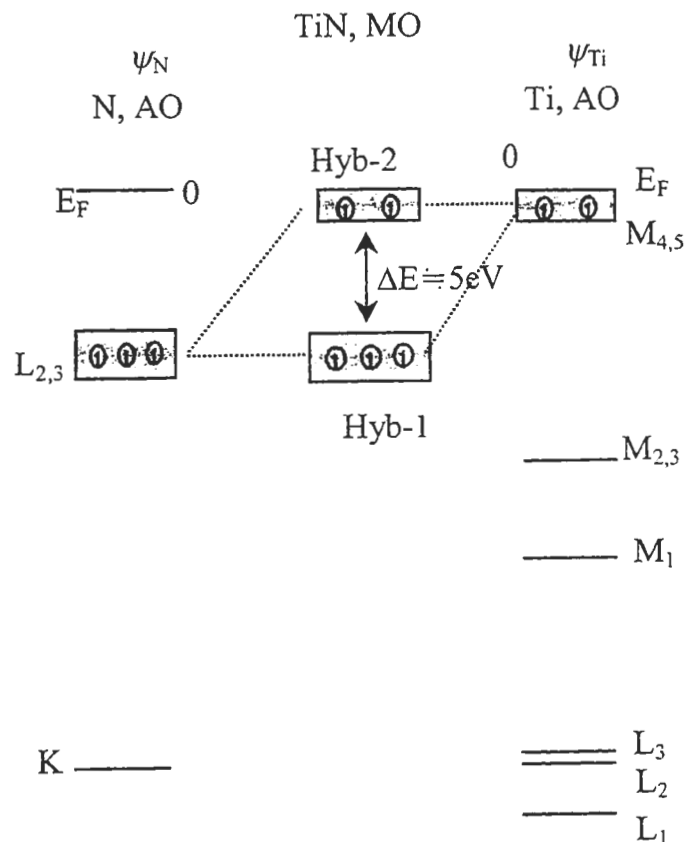


Fig. 2 Schematic drawing of the model of the valence band structure of TiN .

Because the TFA is computation on the spectral data set, the results obtained from “black box” operations might be containing the artifact such as unexpected shoulder peaks. However, this spectrum has recorded in the high-energy resolution mode, it can be considered that these fine structures of the N $KL_{23}L_{23}$ peak in Fig.1 appeared by the result of a hybridization of L_{23} level with Ti $3d$ valence electrons. The electric structure of the valence band on Ti metal and Ti compounds (TiN, TiC, TiO_x) have been discussed using density of states calculation [13,14,15] and direct measuring by XPS/UPS [16,17] in many reports. Based on these investigations, this paper offers following simple model of the valence band structure of TiN(Fig. 2).

Figure 2 shows the schematic drawing of the band structure of N, Ti atomic orbital and TiN molecular orbital. Focusing on the valence electrons of each atom, two electrons occupy $3d(M_{45})$ band for Ti atom and three electrons for N atom occupy $2p(L_{23})$ band that is locating at little below E_F . When the TiN is composed, it can be considered that those valence electrons of N and Ti atom form the hybrid orbital of N $2p$ and Ti $3d$ (a linear combination of N and Ti atomic orbitals) for TiN in term of molecular orbital theory[18]. In addition, it is known that the crystal structure of the TiN is NaCl(the octahedral structure) structure[19]. In this case, five valence electrons from N and Ti atom do not form a single band, i.e., an energy split in two states occurs in the hybridized band and three of five electrons that have same spin direction occupy bonding

orbital($Hyb-1$) and two electrons that also have same spin direction occupy anti-bonding orbital($Hyb-2$). This consideration is actually confirmed in the experimental data. Haupt *et al.* [20] have reported the peak split in the Ti $L_3M_{23}M_{45}$ (peak at 420 eV) region with increasing N concentration that reflects the Ti partial density of states in the valence band(M_{45}). Our experimental data in this energy region showed similar spectral shape. The energy split (ΔE) is estimated about 5 eV from both experimental data [20,21] and calculation [15]. Next step is to estimate the N KLL Auger intensity and relative energy difference from the model of Fig.2. As shown in Fig.2, when the TiN is composed, it can be considered that the KLL transition takes three ways combinations between the hybridized orbitals, $KL_{hyb-1}L_{hyb-1}$, $KL_{hyb-1}L_{hyb-2}$ and $KL_{hyb-2}L_{hyb-2}$ respectively. Based on this consideration, expected relative intensities and energies of above transitions are summarized in Table 2. Since the binding energy of the $hyb-2$ orbital is

N $KL_{hyb}L_{hyb}$ transition of TiN		
Possibilities	Total Intensities	Energy Difference
$KL_{hyb-2}L_{hyb-2}$	1	} $\Delta E \cong 5eV$
$KL_{hyb-1}L_{hyb-2}$	6	
$KL_{hyb-1}L_{hyb-1}$	3	

Table 2 Combinations of Auger transition peaks and relative energy differences of the peaks predicted by the TiN molecular orbital model shown in Fig. 2.

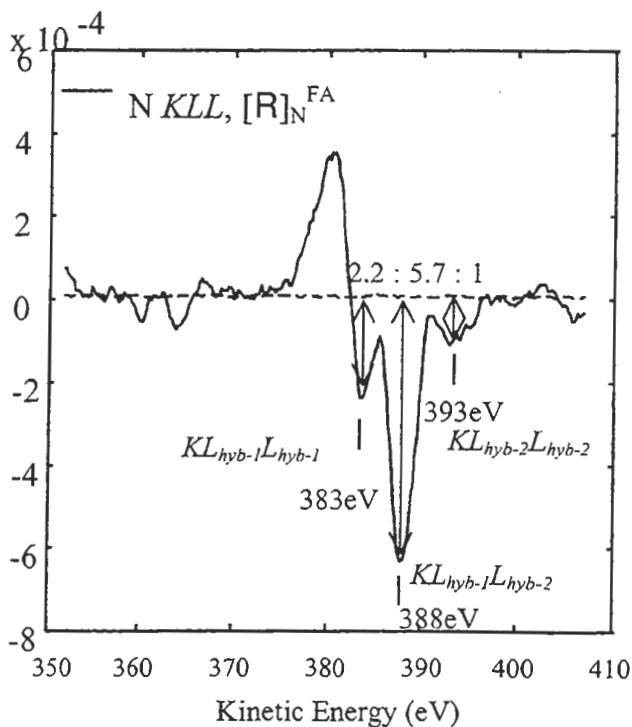


Fig. 3 The assignment of the origin of the shoulder peaks on mathematically extracted N KLL peak using simple model shown in Fig.2.

smaller than $hyb-1$ orbital, the order of Auger energy is considered as $KL_{hyb-2}L_{hyb-2} > KL_{hyb-1}L_{hyb-2} > KL_{hyb-1}L_{hyb-1}$ in kinetic energy.

Figure 3 shows the assignment of the transitions and intensities from table 2 on the target factor analysis result shown in Fig.1. The intensity ratio of each transition on this peak is shown in Fig.3. Although the observed intensity ratio is slightly different from those in Table 2 because of simple peak height measurement, predicted energy differences are considered to be in good agreement with those in Table 1.

4, Conclusion

This paper attempted to explain the physical meaning (real existence) of the shoulder peaks that were observed on the N *KLL* peak extracted by target factor analysis on TiN Auger spectra measured in the high energy resolution mode. To explain the origin of these peaks, a simple model of the electric structure in the hybridized valence electrons of TiN was proposed. Based on this model, possible combinations of the Auger transitions, the intensities and relative energy differences were compared with the spectrum extracted by TFA. The intensity ratio of each peak observed on the spectrum was slightly different from the predicted value from the model, however, the assignment of each peak and relative energy difference in the numerically extracted N *KLL* peak was enough explainable for the existence of the real peaks.

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