The method described can be applied to all metal, semiconductor, alloy ot dielectric thin films. Recent results in the field of ion etching, formation and shaping of thin film circuits in microelectronics and ion beam machining have shown the necessity for the sputtering yield data for various thin films.

TABLE I

Sputtering yields for thin films S_{TF} (at/ions)

Bomb. cond.	Target	Thickness (Å)	Our results	S for solid targets
500 eV A^+	Ti	100	0.68	0.50
1500 eV A^+	Ti	200	1.00	0.70
450 eV A^+	Au	270	2.30	2.20
1500 eV A^+	Au	200	4.20	3.50
450 eV A^+	Ag	200	3.40	2.90
1500 eV A^+	Ag	150	6.20	4.50
450 eV A^+	W	250	0.60	0.54

References

1) H. G. Scott, J. Appl. Phys. **33** (1962) 2011;
2) A. Benninghoven, Z. Angew. Phys. **27** (1969) 51;
3) P. Bowden and D. Brandon, Phil. Mag. **8** (1963) 935;
4) H. Diepers, Phys. St. Solidi, **24**, (1967) 235 and 623;
5) B. Navinšek and G. Carter, Appl. Phys. Letters **10** (1967) 91;
6) B. Navinšek and G. Carter, Can. J. Phys. **46** (1968) 719;
7) B. Navinšek and G. Carter, Int. J. Electronics **22** (1967) 421;
8) G. K. Wehner, Mills Report 2309, Minneapolis, Minnessota (1962);
9) B. Navinšek, Ph. D. Thesis, University of Ljubljana (1968).

2.11 Mass analysis of positive and negative secondary ions emitted from NaCl and KCl monocrystals bombareed by 40 keV argon ions

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The spectra of positive and negative secondary ions were measured from NaCl and KCl monocrystals bombarded by 40 keV Ar^+ ions. The magnet analyser was used. It was found that the secondary ion emission from these dielectrics was identical with the metal and semiconductor emission. The yield of the positive secondary ions is proportional to the reciprocal value of $(I—\Delta I—\Phi)$, i.e. reciprocal value of the difference between the ionization energy and the

work function. The yield of the negative ions is proportional to the reciprocal value of ($\Phi - A$), i.e. reciprocal value of the difference between the work function and electron affinity. The yield of the secondary ion species is not proportional to the corresponding atom concentration in targets.

1. Introduction

Most of the experiments with ion bombardment of dielectrics were aimed at the determination of the sputtering coefficient[1–3] or the etching of the surface[4–7]. The total coefficient of the ion emission as well as the secondary ion species were determined by the time-of-flight method,[8–10] which gives only a rough image of the ion species. The most complete analysis of secondary ions from dielectrics was done by using a magnetic analyser[11,12]. On the other hand, the spectra and yields of scattered[13] and sputtered[14] secondary ions from pure metals and the oxides of these metals — dielectrics — were compared. The only difference in the spectra of the scattered secondary ions from those two targets is the increased yield of some of ion species from oxide layers. However, in the spectra of the sputtered secondary ions from oxide layers there is a greater number of ion species, than from pure metallic surfaces; some peaks are increased. The increase in the yield of positive ions from oxide layers was explained by some authors by the appearance of a forbidden zone 1—2 eV wide, which reduced the probability of neutralization of secondary ions[14]. We believe that the increase in the yield of secondary ions from oxide layers is a consequence of the higher work function of the surface. This conclusion is supported by the fact that no difference was observed in the yields of secondary ions from semiconductors (Si and Ge) and metals[14–16].

2. Experimental results and discussion

The targets were bombarded by 40 keV Ar^+ ions, incident angle was 45°. The density of the primary ion current was cca 100 μA/cm^2, and the residual pressure 5×10^{-6} torr. The other experimental conditions were the same as in our earlier work[16] with metals and semiconductors. The detection of the spectra and the measurement of the yield and energy distribution is made difficult by the charge up of the bombarded surface in the course of bombarment by a high energy ion beam. In order to avoid this effect a fine platinum grid was placed over the bombarded NaCl and KCl surface (Pt Ø 25μm). Because of the small surface of the platinum grid the yield of Pt^+ ions was negligible, and did not influence the accuracy of the measurements. The experimental conditions in these measurements were the same as in earlier measurements with metals and semiconductors, making, therefore, the comparison of these results possible. However, in order to check it in this last experiment also an Al target was bombarded under the same conditions. It is interesting to note that the measured density of the primary ion beam on mentioned dielectrics was less than on Al target. The suppression voltage in all cases was —20 V. The measured intensity of the primary ion beam was 4 times smaller on NaCl and 2 times smaller on KCl than on Al target. The reason for this measured ion beam current reduction is the large coefficient of positive secondary ion emission from these two targets. Under the said conditions of bombardment the coefficient of the secondary ion emission K_+ is of the order of

10^{-1} and therefore, it can noticeably influence the accuracy of the measurement of primary beam intensity. Such a large coefficient of the secondary ion emission, K_+, can be expected from metallic targets only, if during bombardment its surface is covered with an oxide layer. This is the case with metals that have large affinity towards oxygen such as magnesium, aluminium, molibdenum, etc. The emission of the negative secondary ions compensates to a certain degree for the error in measurement resulting from emission of the positive secondary ions. That compensation can be seen on KCl, as the coefficient of the negative secondary ion emission, K_-, is of the same order of magnitude as that one of the positive secondary ions emission (the relation K_-/K_+ is approximately 2/5).

The results of these measurements are shown in Table I for NaCl and in Table II for KCl. Only the highest peaks in the spectra of the secondary ions are tabulated. The same as from metallic and semiconductor targets, besides of secondary ions of the atoms of crystal lattice, also surface impurities and molecular ions have been detected. Numerous ion species are present in the spectra ions of both targets. The highest peaks in the spectra of secondary ions are Na^+ from NaCl and K^+ from KCl. The intensities of these two peaks are very large being almost of the same magnitude as Al^+ (1720 arb. units) from the polycrystalline Al target bombarded under the same conditions. In this case Al target was covered by an oxide layer, and the Al^+ intensity was larger for an order of magnitde than from the pure aluminium surface.

It is known that for Al the difference of the ionization energy and the surface work function is rather small, $(I-\Phi=5.98-4.08=1.90\,\mathrm{eV})$ For the oxide layer is even smaller. For Na on NaCl this difference is $5.12-4.48=0.64\,\mathrm{eV}$[17], and for K on KCl it is $4.32-4.08=0.24\,\mathrm{eV}$. These differences are much smaller than for metals, and it is certainly the main reason for the large coefficient of the positive secondary ion emission from NaCl and KCl. This coefficient for NaCl and KCl under the said conditions is of the order of $10^{-1}\div 1$, while for most of metals and semiconductors it is of the order of $10^{-2}\div 10^{-3}$[14-16]. The peak intensity of the secondary ions K^+ higher than of Na^+, as well as the smaller difference $I-\Phi$ for KCl than it is for NaCl are in agreement with the conclusion obtained for metals and semiconductors[16]. According to that conclusion the coefficient of the secondary ion emission is inversly proportional to the differenre $I-\Delta I-\Phi)$, where $I-\Delta I$ is the particle ionization energy near ath surface; Φ is the work function. It should be pointed out that the correction of the ionization energy near the surface is $\Delta I_{\mathrm{dielectric}} < \Delta I_{\mathrm{semiconductor}} < \Delta I_{\mathrm{metal}}$. Therefore, we can conclude that there is no defference in the emission of secondary ions from these three types of targets: metals, semiconductors and dielectrics.

As it is known from earlier measurements[1] the sputtering cooefficient of KCl is cca two times larger than for NaCl. The same type of positive ions were obtained in our measurement from both NaCl and KCl, but the intensities of those obtained from KCl are in all cases more than two times larger than those from NaCl. That difference is particularly noticeable for Cl^+ ions.

The spectra of negative secondary ions differ not only in respect to peak intensities but also the number of ion species is different. The OH^-, C_2^- and C_2H^- ions were not detected from NaCl, but the corresponding peak intensities from KCl were relatively large. What surprises most is the difference in the Cl^- peak intensities from these targets. The Cl^- peak intensity from KCl is 35 times larger than from NaCl, although the sputtering coefficients of those two targets differ only by factor 2. That surprisingly big difference in the yield of the Cl^- ions could be understood as due to the dependence between the coefficient of the negative ion emission for metals and semiconductors[16)] and reciprocal value of the magnitude $(\Phi - A)$; A is the electron affinity. The atoms of Cl have distinctly large electron affinity ($A = 3.62$ eV) forming easily negative ions Cl^-. The difference $\Phi - A$ is not the same for these two targets; (it is 0.86 eV for NaCl and 0.46 eV for KCl). The negative ions of Cl^-, as well as all other types of negative ions, are formed more easily on KCl than on NaCl. The reason for it is the lower work function of KCl. The difference of this two work functions of 0.4 eV could influence considerably the emission of different types of negative ions. Their yields from the targets would be higher the larger is the electron affinity of sputtered particles.

A great number of research workers tend to find out the chemical properties of bombarded targets by using a mass spectrometer and registering the spectra of secondary ions. One starts from the assumption that the yields of some types of secondary ions should be proportional to the concentration of these elements in an investigated sample. Past measurements showed that this method could be very efficient in detection of elements with a low ionization potential (alkali metals, aluminium, magnesium, etc). On the contrary, it is very difficult to detect elements whose ionization potential is high, such as gold and zinc.

The formation of negative ions is much easier if the atoms of a certain element have larger electron affinity. Therefore, halogen elements could be easily detected in the negative ion spectra, even if only their traces are present.

The result of the bombardment of phosphorus glass[12)] is very instructive. There is the same number of aluminium and phosphorus atoms in that kind of glass. Therefore, the number of sputtering atoms should be the same. However, in the secondary ion spectra Al^+ peak is over 100 times more intensive than P^+ peak. In another kind of glass the atoms of oxygen are 50 % of the total number of atoms, but O^+ peak was hardly measurable, whereas the peaks of secondary ions of other components were more intensive. The measurements of the secondary ion spectra from different metals of standard quality, and different kinds of glass, showed similar results[11)].

NaCl and KCl targets are very convenient for the investigation of the efficiency of secondary ion emission of the elements that form these two compounds. Neglecting the lattice and surface impurities the same number of atoms of alkali element (sodium or potassium) and Cl can be found in them. However, by comparing the yields, in Tables I and II, of Na and Cl secondary ions, as well as of K and Cl ions one can find that they differ a great deal. That difference in case of the NaCl target is larger than 50 times. Whereas for Na and K a very intensive peak of positive ions is dominant, the majority of Cl ions is negative. Such behaviour of the secondary ions of these elements is quite understandable considering the importance of the surface work function, ionization energy and electron affinity on the formation of secondary ion emission.

It could be concluded that the analysis of different solid targets by ion bombardment is very convenient for the detection of elements with low ionization potential, even in case of their small concentration. A quantitative chemical analysis of the targets in general is not possible, for it happens often that some impurity of negligible concentration forms a more intensive peak of secondary ions than an element whose concentration is large, but its ionization potential is high. Therefore, the qualitative analysis is possible but incomplete. The quantitative analysis would be possible only for alloys and compounds of a group of related elements with similar ionization potential and electron affinity. However, the most effective analysis would be achieved by comparison of the secondary ion spectra of the investigated target with the type-spectra obtained from targets of well-known chemical structure under the same bombardment conditions. The secodary ion spectra could also help in estimation of the degree of coverage by adsorbed gases or for detecting the presence of oxide and carbide layers on the target surface.

TABLE I

Ions from a sodium chloride

Mass No.	Positive		Negative	
12	C	1.2	C	1.8
13			CH	0.6
16	O	1.1	O	3.0
23	Na	1170.0		
35	Cl	5.1	Cl	15.4
37	Cl	1.7	Cl	5.3
39	NaO	3.2		
46	Na_2	52.5		
58	NaCl	3.7		
60	NaCl	1.2		
62	Na_2O	68.0		

Ions from an aluminium: Al^+ (1720), C^- (12), O^- (300).

TABLE II

Ions from a potassium chloride

Mass No.	Positive		Negative	
12	C	4.0	C	7.2
13			CH	8.0
16	O	2.3	O	13.0
17			OH	7.1
23	Na	3.3		
24			C_2	17.0
25			C_2H	14.0
35	Cl	48.0	Cl	547.0
37	Cl	16.0	Cl	175.0
39	K	2760.0		
55	KO	7.7		
78	K_2	122.0		
94	K_2O	202.0		

References

1) B. Navinšek, J. Appl. Phys., **36** (1965) 1678;
2) A. I. Akišin, S.S. Vasiljev and L. N. Isaev, Izv. AN SSSR, ser. fiz., **26** (1962) 1356;
3) R. L. Hines and R. Wallor, J. Appl. Phys., **32** (1961) 202;
4) G. V. Spivak et al., Dokl. AN SSSR, **114** (1957) 1001;
5) A. I. Krohina et al., Izv. AN SSSR, ser. fiz., **23** (1959) 741;
6) A. I. Krohina et al., Izv. AN SSSR, ser. fiz., **27** (1963) 1224;
7) C. M. Drum, Phys. Stat. Sol. **9** (1965) 635;
8) G. M. Batanov, Soviet Phys. — Solid State, **3** (1961) 642;
9) G. M. Batanov, Soviet Phys. — Solid State, **4** (1962) 1778;
10) I. A. Abrojan and V. P. Lavrov, Soviet Phys. — Solid State, **4** (1962) 3254;
11) H. I. Liebl and R. F. K. Herzog, J. Appl. Phys., **34** (1963) 2893;
12) J. T. Kerr, 15 th Annual Conference-Mass Spectrometry — Denver, May 14—19, (1967) p. 318;
13) C. Snoek, Thesis (1966);
14) J. F. Hennequin, Thesis, Université de Paris (1968);
15) H. E. Beske, Z. Naturforschg., **22a** (1967) 459;
16) Z. Jurela, Atomic Collision Phenomena in Solids, Proceedings of the International Conference, Brighton, North-Holland Publishing Company (1970) p. 339;
17) B. Ja. Mojžes, Fizičeskie processi v oksidnom katode, Izdateljstvo „Nauka“, Moskva (1968).

2.12 The sputtering of alkali halide surfaces with low energy irradiation

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In alkali halide crystals it is possible to transfer energy from incident electrons or photons to single lattice atoms with extremely high efficiency and produce defects in the material. Several models for the transfer process have been proposed and there is now strong evidence to support those of Pooley and Hersch[1,2]. Briefly their models proceed by (*i*) excitation of a halogen ion in the lattice to a higher state, (*ii*) movement of the central portion of the ion to an adjacent site with the formation of a molecular ion and (*iii*) a return to the new ground state. In this last stage the excess energy is imparted as kinetic energy to the molecular ion and is sufficient to dissociate the molecular ion and initiate a replacement collision sequence to separate the vacancy and interstitial. The collision chain is propagated along a line of similar atoms (in this case a $\langle 110\rangle$ direction) and one expects that if the chain reaches the surface the last atom will be ejected with momentum along the $\langle 110\rangle$ direction.

Alternative theories of Varley, Klick, Williams[3] would also produce ejection from the surface in the $\langle 110\rangle$ direction but they require more energy for the first stage since they consider this as an ionisation or multiple ionisation of a