phys. stat. sol. (a) **93**, 559 (1986)

Subject classification: 61.70; 78.70; S1.2

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# The Effect of Deposition Temperature on the Defect Structure of Ni Electrodeposits Studied by Positron Annihilation

By

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The effect of deposition temperature on the defect structure of Ni electrodeposits is studied by positron lifetime and Doppler broadening spectroscopy. The results indicate that positron trapping is dominated by monovacancies and H bubbles in Ni electrodeposits. Surprisingly strong variation of the positron trapping rates with deposition temperature is interpreted as H escape from vacancies and bubbles during the course of deposition.

Mittels Positronenlebensdauer und Dopplerverbreiterungsspektroskopie wird der Einfluß der Niederschlagstemperatur auf die Defektstruktur von Ni-Elektroniederschlägen untersucht. Die Ergebnisse zeigen, daß Positronenanhaften durch Monovakanzen und H-Bläschen in Ni-Elektroniederschlägen gesteuert wird. Die überraschend starke Änderung der Positronenanhaftraten mit der Niederschlagstemperatur wird als H-Befreiung aus Leerstellen und Bläschen des Niederschlagsprozesses interpretiert.

## 1. Introduction

The structure, physical, and mechanical properties of metallic electrodeposits are strongly dependent on the plating conditions such as bath composition, cathode current density, temperature, pH, solution agitation, and also to some degree on the nature and structure of the substrate and on the thickness and age of the deposits [1]. During the course of deposition inevitably great number of non-equilibrium lattice defects are incorporated into the deposits. However, the defect structure of electrodeposits is not well understood at present and poses several open questions. Particularly the influence of lattice distortions and gas impurities on the mechanical properties of the deposits is of great importance. It is well documented that high tensile and compressive internal stresses are accumulated during the growth of electrolytically obtained metallic films. The decrease of the internal stress with increasing deposition temperature sometimes has been attributed to the decreasing H content of Ni electrodeposits [1]. Introduction of a H atom at an interstitial site in the crystal causes a local distortion of the lattice and builds up local strain and stress fields and in general is accompanied with the increase of the lattice volume [2]. However, taking into consideration the low solubility [3] and high diffusivity [4] of H in Ni at or above room temperature it is hard to believe that interstitially dissolved H is responsible for the high internal stresses at low deposition temperatures in electrodeposited Ni. It is well known, on the other hand, that H may be trapped in a variety of sites in real metals. Trapping in vacancies, vacancy clusters, voids, dislocations, dislocation loops, grain boundaries, strain fields, and at impurities results in an enhanced solu-

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bility of H in a number of metals [5]. The presence of trapped H in lattice defects may be responsible for striking mechanical effects like H embrittlement [6].

Techniques of positron annihilation have gained widespread application in experimental defect spectroscopy in the past few years [7]. Here we applied positron lifetime spectroscopy and Doppler broadening technique to characterize lattice imperfections and to study the influence of deposition temperature on the defect structure in Ni electrodeposits.

## 2. Experimental

The conditions of electroplating are given in Table 1. The Ni layers were deposited on Cu substrate to a thickness of about 200 μm. The measuring techniques (lifetime and Doppler broadening) applied and the data treatment have been described in detail elsewhere [8, 9]. All the measurements were carried out at room temperature.

Table 1
Composition of the plating solution and deposition conditions

| composition of the plating bath | electrolyte concentration ($g/dm^3$) | current density ($mA/cm^2$) | pH |
|---|---|---|---|
| $NiSO_4 \cdot 7\ H_2O$ | 170 | | |
| $NiCl_2 \cdot 6\ H_2O$ | 35 | 50 | 5.6 |
| $H_3BO_3$ | 35 | | |
| $Na_2SO_4 \cdot 10\ H_2O$ | 70 | | |

## 3. Results and Discussion

Analysis of the lifetime spectra showed the existence of two lifetime components ($\tau_1, \tau_2$), where the longer lifetime $\tau_2$ was independent of the deposition temperature and equals $\tau_2 = (335 \pm 15)$ ps. In order to compare the Doppler broadening and lifetime results we calculated the mean lifetime $\bar{\tau} = \tau_1 I_1 + \tau_2 I_2$ ($I_1$, $I_2$ are the relative intensities of the lifetime components). The results of the Doppler broadening and positron lifetime measurements are given in Fig. 1.

The structure of the lifetime distributions indicates that at least two types of lattice defects were created during the course of deposition. The value of the first lifetime ($\tau_1$) falls well above the value characterizing positron annihilations in undefected, crystalline Ni, $\tau_c = 110$ ps [10], however, never exceeds the lifetime of positrons trapped in monovacancies, $\tau_v = 180$ ps [10]. This lifetime component seems to be an average of annihilations from untrapped state and positron traps, like monovacancies, dislocations, etc. The longer lifetime component ($\tau_2$) could be attributed to positrons localized in some spatially more extended lattice defects with deeper electronic potential.

In a recent isochronal recovery study of Ni electrodeposits obtained at 45 °C under the same plating conditions we found a variation of $\tau_2$ in the 325 to 445 ps range [8]. These lifetime values as compared with the recently calculated positron lifetimes in vacancy clusters in Ni [11] suggest that open-volume defects corresponding to the longer lifetime component might have a volume of ten or more vacancies. It is well known, on the other hand, that electrolytically obtained metallic films contain a considerable amount of microvoids partly filled with H atoms [12]. TEM studies showed that these so-called "H bubbles" were mainly formed along grain boundaries in metallic electrodeposits [13]. The shorter lifetime value showed saturation at 180 ps,

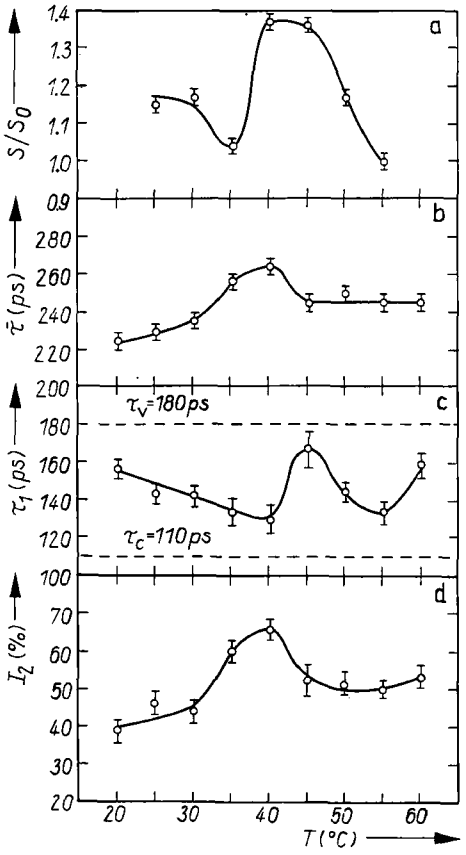


Fig. 1. a) $S$-parameter, b) mean lifetime, c) lifetime $\tau_1$, and d) relative intensity $I_2$ as functions of deposition temperature $T$. $S_0$ represents the $S$-parameter for a sample deposited at 50 °C. The curves shown serve as a guide to the eye only

i.e. at the lifetime value characteristic of vacancies in Ni, as the result of isochronal heat treatments [8].

These observations lead us to the conclusion that the shorter lifetime component in our measured spectra corresponds mainly to monovacancies, while open-volume positron traps responsible for the appearance of the longer lifetime component are likely to be H bubbles. It should be emphasized, however, that contributions to the lifetime components from other defects such as dislocations and dislocation/vacancy loops could not be excluded.

In order to conclude on the different processes influencing the development of the defect structure during the deposition process we applied a simple three-state positron trapping model to analyse our data. We assumed in the model that vacancies and H bubbles were the dominant positron traps and neglected the contribution of other positron traps to the measured annihilation parameters. Under certain assumptions discussed in [14] we could use the following equations to calculate positron trapping rates of vacancy ($K_v$) and H bubble ($K_b$) trapping from the measured quantities ($\tau_1, \tau_2, I_1, I_2$):

$$K_v = \frac{\tau_1(\tau_c^{-1} - I_2\tau_2^{-1}) - I_1}{\tau_v - \tau_1},$$

$$K_b = \frac{I_2}{I_1}(\tau_c^{-1} - \tau_2^{-1} - K_v).$$

The results are shown in Fig. 2.

Before we turn to the analysis of the deposition temperature dependence of positron trapping rates let us discuss the factors influencing the magnitude of trapping rates.

Firstly it is now well established that the positron trapping rate is proportional both to the defect concentration (at least if the defect concentration is not too high) and roughly to the defect volume [7, 15]. Therefore, a decrease of the trapping rate might correspond to a decrease of the defect concentration or/and sizes.

Secondly decoration of defects with light impurities (H, D, He, Li, C, N, etc.) influences both the trapping rate and the annihilation characteristics of positrons trapped in such defects. The resulting positron annihilation parameters (lifetime,

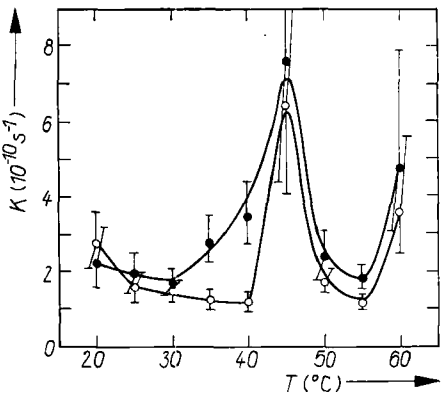


Fig. 2. The positron trapping rates for vacancy $K_v$ (○) and H bubble trapping $K_b$ (●) as functions of deposition temperature $T$. The curves shown are only guides to the eye

$S$-parameter, etc.), binding energy, and hence the positron trapping rate depend on the nature of the impurities, interactions of impurity atoms with the matrix atoms at the defect surface, impurity density inside the defect, etc. Unfortunately the effect of gas impurities on the trapping and annihilation properties of positrons in lattice defects is not well understood at present, despite considerable theoretical efforts. Several attempts have been made to account for the influence of H decoration on the positron lifetime and binding energy in vacancies and small vacancy clusters in metals [11, 16 to 19]. Reliable quantitative results have not been obtained yet, but some qualitative trends appear in these calculations. An agreement has been reached that H decoration generally reduces both the positron lifetime and binding energy in the case of monovacancies. However, the decorated vacancies even with more than one H atom are still effective traps of positrons.

Recently Hansen et al. [19] have shown that the calculated positron lifetimes are not too sensitive to the applied charge density distributions in the calculations. The lifetime of positrons bound to vacancies in Ni decorated with single H atoms in a realistic highly off-centre position in the vacancy was only moderately decreased by the presence of the H atom. The magnitude of the positron binding energy, on the other hand, is strongly model dependent, therefore, it is hard to draw conclusions regarding the behaviour of the positron trapping rate [19].

As we shall see below the presented interpretation of the observed trapping rate variations in our experiments is consistent with the assumption that H decoration reduces the positron trapping rate both to monovacancies and microvoids in Ni.

The variation of positron trapping rates with deposition temperature poses the following possible picture on the defect structure and the interaction of H with open-volume defects in Ni electrodeposits at different deposition temperatures. The decrease of the positron trapping rates and the $S$-parameter in the 20 to 30 °C temperature range may be due to the decreasing amount of incorporated vacancies and H bubbles in the deposits with increasing temperature in agreement with other observations [1]. This is a natural consequence of the increasing diffusivity of Ni atoms with temperature. The higher mobility of Ni atoms and lattice vibrations facilitate the reorientation, relaxation, and coalescence of small atomic clusters during the course of film growth at higher temperatures. This results in a more homogeneous structure of the deposits and decreasing amount of lattice defects retained in the films at higher temperatures. The increase of the positron trapping in H bubbles ($K_b$) above 30 °C could be attributed to H escape from the bubbles. The mobility of H atoms is higher at higher temperatures both in the liquid and solid phases. The increased mobility increases the probability of H escape from the solid. Furthermore the higher temperature facilitates thermal detrapping of bound H atoms from lattice defects. Effective H detrapping could be responsible for the increase of the trapping rates both to vacancies and bubbles at around 45 °C. The reduced shielding of the defect

potentials results in a pronounced increase of the positron trapping rates $K_v$ and $K_b$ at this temperature. This temperature corresponds to a H binding energy of about 0.55 eV which is in remarkable agreement with the experimentally found deuterium and theoretically estimated H binding energy to He bubbles in α-irradiated Ni [20].

The dependence of the $S$-parameter on the deposition temperature resembles that of $\tau_1$ rather than $\bar{\tau}$. The striking similarity between the two curves suggests that the behaviour of the $S$-parameter is dominated by the positrons trapped in vacancies. The contribution of H bubbles becomes significant if the positron trapping in these defects increases considerably. This indeed explains the observed variation of the $S$-parameter in the temperature range 35 to 45 °C. At 35 °C $S$ decreases in accordance with $K_v$, while it increases considerably at 40 °C where $K_b$ increases significantly possibly due to H escape from the bubbles. At 45 °C positron trapping in vacancies increases and prevents the further increase of the $S$-parameter. H escape increases the mobility of Ni ions and facilitates the relaxation of the lattice during the course of film growth. The combined effects of H escape and defect disappearance could be responsible for the diminution of $K_v$ and $K_b$ as well as the $S$-parameter above 45 °C. Escape of more tightly bound H from vacancies and H bubbles may be responsible for the increase of the positron trapping rates at 60 °C.

## 4. Conclusions

In conclusion, the results of the positron annihilation measurements show that among the number of lattice defects formed in Ni electrodeposits during the course of film growth at least two types act as positron traps. These were associated with vacancies and H bubbles along grain boundaries. The concentration of lattice defects incorporated in the electroformed layers decreased as the temperature of deposition rised in agreement with previous observations. One possible explanation for the steep increase of the trapping rates above 30 and 45 °C is H escape from the bubbles and vacancies, respectively. If this interpretation is correct, the results also indicate that several different H bound states exist in the defects resulting in a broad temperature range of H escape from the defects.

Finally it should be emphasized that although the presented interpretation of the positron annihilation results on Ni electrodeposits is quite plausible, it is based on several assumptions regarding positron–defect and H–defect interactions which await confirmation both from theoretical and experimental sides.

***Acknowledgements***

The authors wish to thank Dr. Zs. Kajcsos for stimulating discussions and the Hungarian Academy of Sciences for financial help.

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*(Received November 11, 1985)*