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Characterization of Structural and Dielectric Properties of Silicon Nitride Thin Films Deposited by PECVD

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Abstract— The structural and electrical properties of silicon nitride (SiN_x) are influenced by its composition ratio, x . In this study, we examine the characteristics of SiN_x films, deposited by plasma-enhanced chemical vapor deposition (PECVD), using X-ray photoelectron spectroscopy (XPS), electron microprobe microscopy (EMP), ellipsometry, and high-voltage broadband dielectric spectroscopy (HVBDs). The film composition ranged from N-rich to Si-rich. The dependence of refractive index, permittivity, loss factor and AC conductivity on the SiN_x ratio is presented and discussed.

Keywords—Silicon nitride, SiN_x , Thin-film, PECVD, Refractive index, Dielectric properties, High voltage.

I. INTRODUCTION

Silicon nitride (SiN_x) thin films are widely used in modern technologies because of their wide range of tunable electrical, optical, and mechanical properties including band gap, refractive index, dielectric constant, and stress. They depend on the chemical composition through the deposition conditions [1]. These properties enable applications such as anti-reflection coatings for solar cells, optical waveguides, oxidation masks and encapsulation protection barriers for thin and lightweight electronic devices for long-life flexible displays [2]. In the semiconductor industry, SiN_x layers play a critical role as gate dielectrics for thin film transistors [3]. They also enhance galvanic isolation (used in isolated-gate drivers for electric vehicles) by reducing leakage current by a combination of charge barrier and field grading properties [4]. SiN_x films are usually deposited by plasma-enhanced chemical vapor deposition (PECVD) process. By varying the deposition parameters of the PECVD process, the value x , the N/Si ratio, can be varied and controlled. Hence, a diverse set of structural and electrical properties is obtained [5]. Although the deposition parameters have been widely studied with respect to the stoichiometry [6-8], the influence on the dielectric properties and electrical conductivity is not well established.

This study investigates the relationship between the structural and dielectric characteristics of SiN_x deposited by PECVD under different conditions. This is achieved by controlling the $x=[\text{N}]/[\text{Si}]$ ratio and measuring the physico-chemical characteristics directly from blanket layers of SiN_x deposited on Si wafers. Electrical measurements, for high-voltage broadband dielectric spectroscopy, were obtained from metal-insulator-metal (MIM) capacitor test structures at wafer level. The results will facilitate performance improvements in future electronic devices with higher voltage ratings.

II. EXPERIMENTAL PART

A. Physico-chemical characterization

Blanket layers of $1\ \mu\text{m}$ SiN_x were deposited by PECVD in an industrial production cleanroom facility on 200mm Si wafers with a thickness of $300\ \mu\text{m}$ (see Fig. 1).

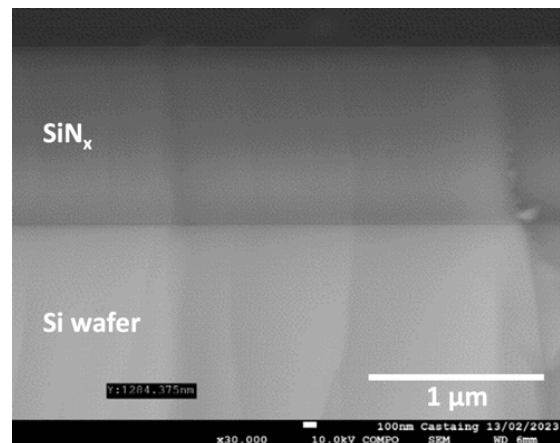


Figure 1. Cross-section SEM image of a blanket SiN_x layer deposited on Si wafer.

To determine their structural properties, they have been physico-chemically characterized using different techniques. X-ray diffraction (XRD) was used to analyze the crystallinity of the SiN_x films, revealing their amorphous nature across all deposition conditions. For the elementary composition, X-ray photoelectron spectroscopy (XPS) was performed using the Kalpha Thermo Scientific XPS system with a source of Al ($h\nu$ 1486.6 eV and at pass energy of 30V for high-resolution spectra (step 0.1 eV) and 160 eV for general spectra (step 1 eV). This was complemented by Ar ion etching to establish a depth profile, enabling the determination of atomic concentrations within the SiN_x films up to a depth of few tens of nanometers. However, despite its efficiency in assessing the chemical environment, XPS is inherently surface-sensitive and cannot fully analyze a $1\ \mu\text{m}$ -thick, bulk SiN_x layer. A comprehensive elementary characterization was obtained using an electron microprobe (EMP) analysis, employing a field emission gun (Cameca SXFiveFE). This uses an accelerating voltage of 7 kV, a spot size of $10\ \mu\text{m}$ to a depth of approximately 500 nm to quantify the atomic percentages of Si and N in carbon coated SiN_x films. The thickness and

refractive index (RI) were derived from ellipsometry measurements directly performed on the blanket layers.

B. Electrical Characterization

Ten different MIM capacitor test structures were deposited under the same PECVD conditions and manufactured in order to evaluate the effects of changing the stoichiometry $x=[N]/[Si]$ on the dielectric properties. Bottom and top metals used TiW/Au, as shown in Fig. 2. TiW acts as an adhesion layer between SiN_x and Au both at the bottom and top of the SiN_x layer. Additionally, the MIM structure is symmetrized by the TiW layers surrounding the SiN_x to ensure a work function symmetry for the high voltage characterization. A thick top Au metal has been electroplated where the electrical contact will be made through needles with the electrical source in order to avoid mechanical degradation on the SiN_x layer. Finally, the MIM test structures were encapsulated with a capping polyimide that also served as mask to wet-etch the SiN_x layer and uncover the bottom metal contact.

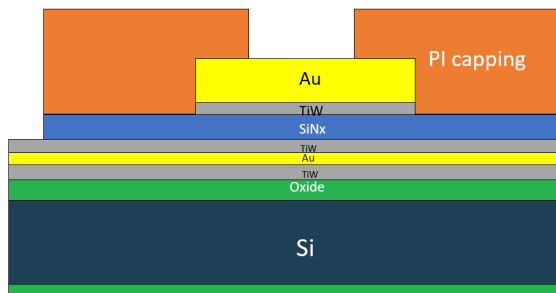


Figure 2. Cross-section sketch of metal-insulator-metal capacitor wafer-level test structure.

High voltage broadband dielectric spectroscopy (HVBDS) tests were performed at room temperature to determine the dielectric properties (permittivity and loss factor) and AC conductivity of each different MIM capacitor structure by applying AC voltages between 1 V_{rms} and 400 V_{rms} in a frequency range from 100 mHz up to 1 kHz. More details on this measurement have been reported elsewhere [9, 10].

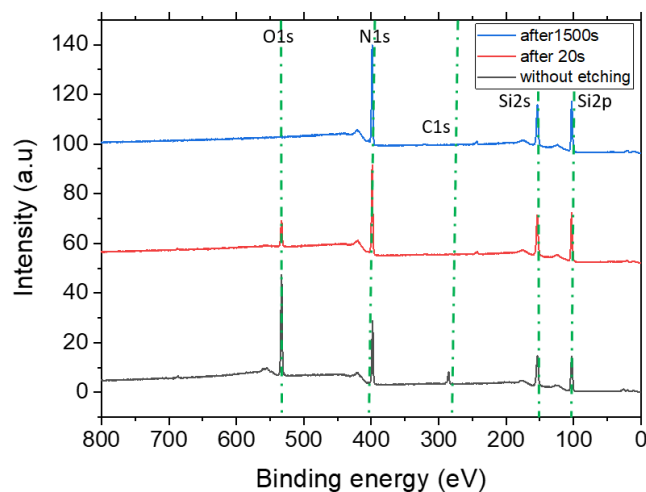


Figure 3. XPS survey of a SiN_x layer (sample 1): (1) without etching, (2) after 20s of Ar etching, and (3) after 1500s of Ar etching.

III. RESULTS AND DISCUSSION

A. Composition and Stoichiometry

Three representative XPS spectra from silicon nitride films are shown in Fig. 3, namely (1) without etching, (2) after 20 seconds of etching, and (3) after 1500 seconds of etching. Si, 2p, peaks with high amplitudes at 101.9 eV and N, 1s, peaks at 397.7 eV are observed in the spectrum, indicating the dominant presence of Si and N elements within the film. Additionally, the O, 1s, peak at 532.4 eV and C, 1s, peak at 284.5 eV are related to surface pollution and decrease after Ar ion etching. However, it is important to note the continued presence of structural oxygen at larger depths within the films that disappears at about 150 nm from the surface. The $x=[N]/[Si]$ ratio was evaluated by EMP FEG at a depth of 500 nm in the different SiN_x layers. This yielded values lying between $x = 0.86$ and 1.50 depending on the deposition conditions, as listed in Table 1. The nitrogen content decreases while the silicon content increases as the deposition conditions are varied from samples 1 to 10. Whereas samples 1 and 2 show a N-rich composition films ($x > 1.33$), samples 4 to 10 are Si-rich films ($x < 1.33$). Despite a slight N excess, sample 3 with $x=1.36$ is the nearest to an ideal stoichiometry for Si_3N_4 , where $x=1.33$.

Table 1. Atomic percentages of N and Si, the N/Si ratio and thickness of the films measured by EMP FEG and ellipsometry, respectively.

Sample#	Atomic% N	Atomic% Si	$x=[N]/[Si]$	Thickness (μm)
1	59.721	39.715	1.50	1.06
2	59.209	40.217	1.47	1.10
3	57.336	42.134	1.36	1.12
4	53.346	46.099	1.15	1.11
5	51.21	48.276	1.06	1.09
6	49.558	49.888	0.99	1.06
7	48.945	50.495	0.96	1.03
8	48.545	50.907	0.95	1.01
9	47.572	51.873	0.91	0.97
10	46.18	53.262	0.86	0.95

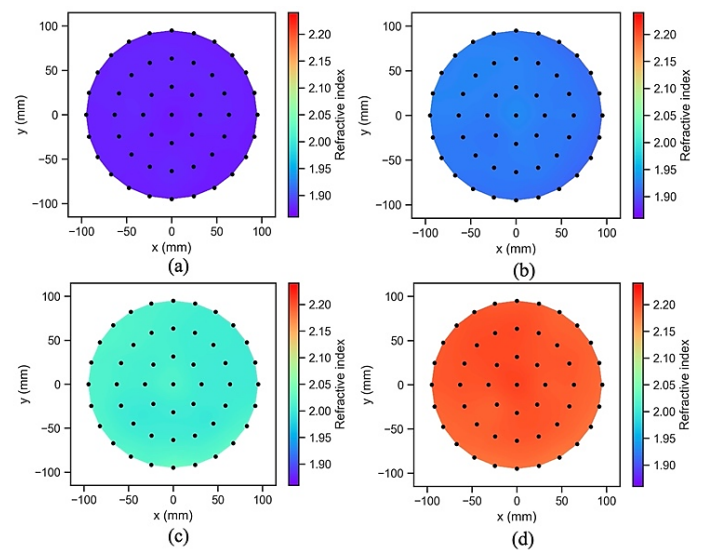


Figure 4. Refractive index variation across the SiN_x layer measured by ellipsometry for two different process conditions: (a) $x=1.50$, (b) $x=1.36$, (c) $x=1.06$ and (d) $x=0.86$. The x-y wafer dimensions are in millimeters.

B. Refractive Index and Thickness

The values of the thickness in Table 1 reduce slightly as the $x=[N]/[Si]$ ratio decreases, but it remains uniform across the entire 200mm wafer at approximately, $1 \mu\text{m} \pm 0.05 \mu\text{m}$. Refractive index maps are shown in Fig. 4 for four different deposition conditions showing a high degree of uniformity and indicative of well controlled PECVD deposition.

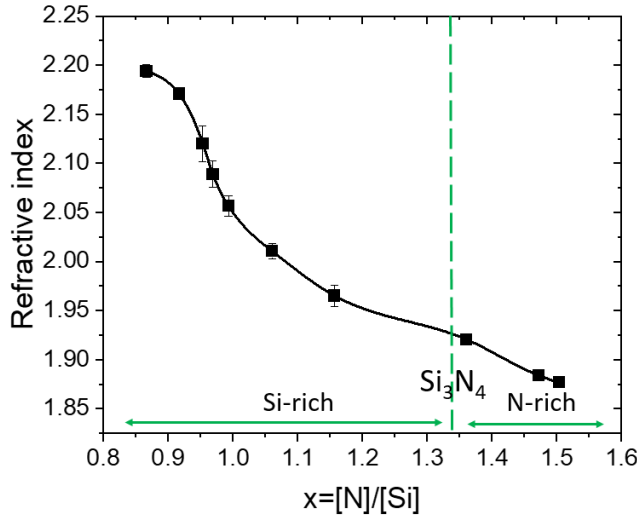


Figure 5. Refractive index variation versus the $x=[N]/[Si]$ ratio.

The RI, measured by ellipsometry, for each $x=[N]/[Si]$ value is shown in Fig. 5. The RI decreases as x increases, as expected, given the reduction in the fraction of the high RI element, Si.

C. Low Voltage Broadband Dielectric Spectroscopy

The influence of the ratio, x , on the permittivity and loss factor for the films is given in Figs. 6. (a) and (b) respectively. Various MIM structures were measured using dielectric spectroscopy at frequencies: 1200 Hz, 600 Hz, 220 Hz, 110 Hz, and 60 Hz using a low voltage of 1V. The sample with the highest silicon concentration ($x=0.86$) gave the highest permittivity (~ 7.2). For Si-rich samples, the permittivity shows a decrease as the parameter x increases and exhibits values between 6.3 and 7.2, which are compatible with what has been found previously in the literature [11]. Notably, the lowest permittivity value (~ 6.25) is observed when x approaches stoichiometry ($x=1.36$). Subsequently, a slight increase is noted in the N-rich region between 6.25 and 6.35, although the permittivity remains comparatively low. The dielectric constant exhibits a clear dependency on the $x=[N]/[Si]$ ratio. The primary reason for this is the variation in bonding type when transitioning from N-rich to Si-rich structures. Hence, the level of nitridation could be estimated by the measurement of the permittivity. The same behavior is observed for all frequencies. On the contrary, the loss factor $\tan\delta$ is frequency dependent but remains more-or-less constant as a function of x ; The loss factor shows its highest value at the highest silicon concentration ($x=0.86$), then decreases and remains constant, before decreasing again for $x<0.9$, with some evidence of a negative trend.

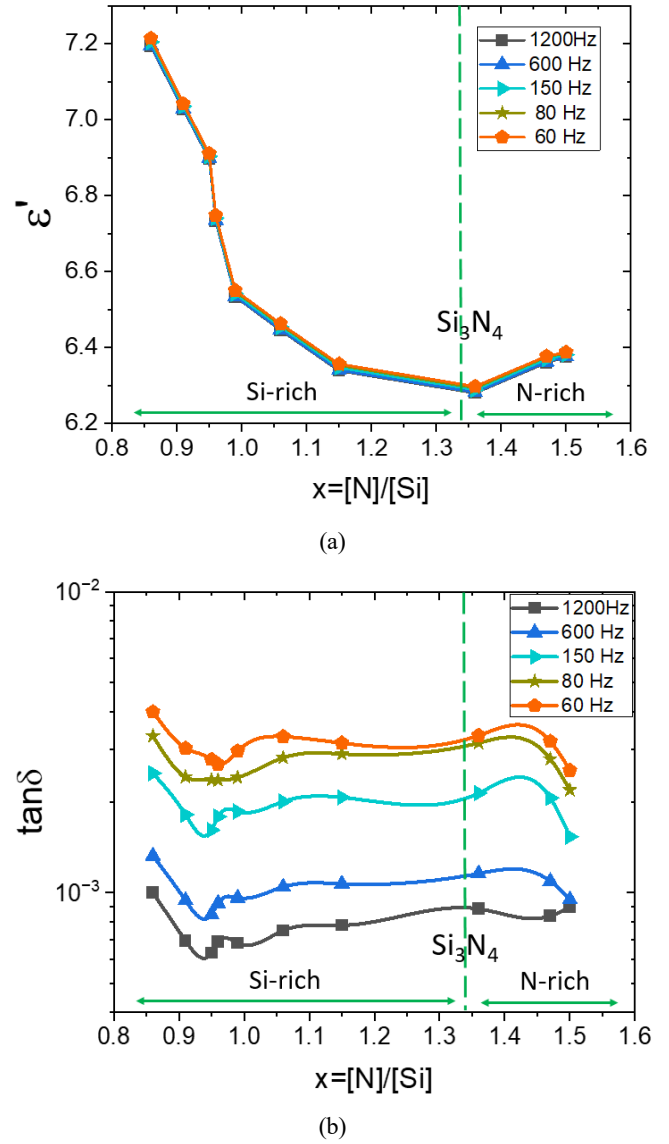


Figure 6. Correlation between (a) the permittivity, (b) loss factor $\tan\delta$ and the $x=[N]/[Si]$ ratio at different frequencies for 1V.

D. High Voltage Broadband Dielectric Spectroscopy

The AC conductivity dependence on the applied electric field is presented in Figure 7 for different x values. Two distinct responses can be identified: linear behavior up to a threshold field, followed by a nonlinear, field dependent, behavior. The N-rich samples exhibit the largest linear regions extending up to a $336 \text{ V}_{\text{rms}}/\mu\text{m}$ threshold field for $x=1.5$ where the applied voltage is extended to $>700 \text{ V}_{\text{rms}}/\mu\text{m}$ to reach the nonlinear region. On the contrary, the Si-rich samples have the shortest linear regions only up to a $92 \text{ V}_{\text{rms}}/\mu\text{m}$ threshold field for $x=0.86$. Figure 8 presents the relationship between the threshold field and the $x=[N]/[Si]$ ratio such that the threshold field increases as x increases, then stabilizes at a constant value in the N-rich regions. The nonlinear behaviour of amorphous silicon nitride is likely to be linked to the variation in the densities of localized states. These may be due to structural irregularities, silicon dangling bonds, or impurities such as hydrogen and oxygen. The states significantly affect the film conductivity [12, 13]. Further study is required to determine the role of the proportion of silicon, nitrogen

dangling bonds and impurities in determining AC and DC conduction mechanisms.

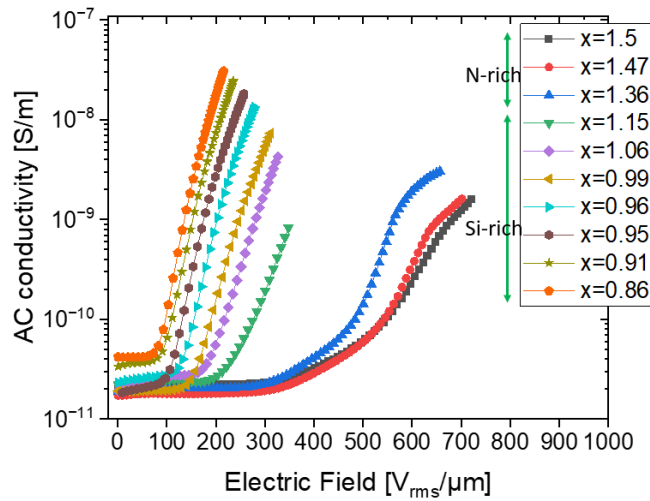


Figure 7. AC conductivity as a function of the electric field at 10Hz for the different x values.

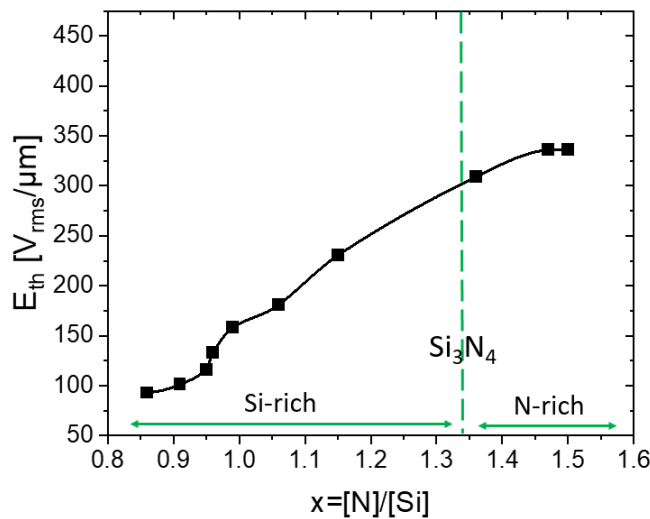


Figure 8. Correlation between the threshold electric field and the $x=[N]/[Si]$ ratio at 10Hz.

CONCLUSION

By varying PECVD deposition conditions, SiN_x layers of different $x=[N]/[Si]$ ratios have been fabricated and evaluated. The intrinsic dielectric properties, including RI, permittivity, loss factor and AC conductivity, were measured as a function of the composition covering compositions from Si-rich to N-rich. Si-rich films, which have the highest refractive indices, exhibit the highest permittivity whereas N-rich films with lower refractive indices show lower permittivity values. AC conductivity measurements, when combined with structural investigations, provide valuable insights and information into charge transfer mechanisms. Higher nitrogen content leads to

a longer transition time to the non-linear AC conductivity region, whereas this transition is shorter for Si-rich films.

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REFERENCES

- [1] M. Gupta, V. K. Rathi, R. Tangaraj, and O. P. Agnihotri, "The Preparation, Properties and Applications of Silicon Nitride Thin Films Deposited by Plasma-Enhanced Chemical Vapor Deposition", *Thin Solid Films* **204**, 77-106, 1991.
- [2] N. Hegedüs, K. Balázs, and C. Balázs, "Silicon Nitride and Hydrogenated Silicon Nitride Thin Films: A Review of Fabrication Methods and Applications", *Materials* **14**, 5658, 2021.
- [3] M. H. W. M. Van Delden and P. J. Van der Wel, "Reliability and electric properties for PECVD a-SiN_x:H films with an optical band-gap ranging from 2.5 to 5.38 eV", *Proc. IEEE International Reliability Physics Symposium (IRPS)*, pp. 293-297, 2003.
- [4] S. Diahm, L. O'Sullivan, E. Ceccarelli, P. Lambkin, J. O'Malley, J. Fitzgibbon, B. Stenson, P.J. Murphy, Y. Zhao, J. Cornett, A. Sow, B. Chen, S. Geary, "Improving Polyimide Isolation Performance by Tailoring Interfaces with Nitride Layers for Digital Isolator Application", *Proc. IEEE International Conference on Dielectrics (ICD)*, pp. 570-573, 2020.
- [5] S. V. Nguyen and S. Fridmann, "Plasma Deposition and Characterization of Thin Silicon-Rich Silicon Nitride Films", *J. Electrochem. Soc.* **134**, 2324, 1987.
- [6] H. Ur Rahman, A. Gentle, E. Gauja and R. Ramer, "Characterisation of dielectric properties of PECVD Silicon Nitride for RF MEMS applications", *Proc. IEEE International Multitopic Conference*, 2008.
- [7] F. Pavlyák, I. Bertóti, M. Mohai, I. Biczó, J. Giber, "AES and XPS characterization of SiN_x layers", *Surface and Interface Analysis* **20**, 221-227, 1993.
- [8] I. Guler, "Optical and structural characterization of silicon nitride thin films deposited by PECVD", *Mater. Sci. Eng. B* **246**, 21-26, 2019.
- [9] S. Diahm, G. Sheehan, K. Bennett, P. Lambkin, M. Canty and B. Chen, "High-Field and High-Frequency Dependencies of Intrinsic Dielectric Properties and Lifetime in Polyimide at Sub-PDIV", *Proc. 4th IEEE International Conference on Dielectrics (ICD)*, pp. 118-121, 2022.
- [10] S. Diahm, P. Lambkin, B. Chen, "Nonlinear Dielectric Properties of Polyimide in High AC Electric Field", *J. Appl. Phys.* **132**, 154101, 2022.
- [11] Thorp, J. S., A. B. Ahmad, B. L. J. Kulesza, and T. G. Bushell. "The permittivity and dielectric loss of reaction-bonded silicon nitride." *Journal of materials science* **19** (1984): 3680-3686.
- [12] H. Sato, H. Kato, Y. Ohki, Kwang Soo Seol, T. Noma, "Electrical properties in silicon oxynitride and silicon nitride prepared by plasma-enhanced chemical vapor deposition", *Proc. IEEE International Symposium on Electrical Insulating Materials (ISEIM)*, 2001.
- [13] K. Czarnacka, F. F. Komarov, I. A. Romanov, P. Żukowski, I. N. Parkhomenko, "AC measurements and dielectric properties of nitrogen-rich silicon nitride thin films", *Proc. IEEE International Conference Nanomaterials: Application & Properties (NAP)*, 2017.